(BuOH), R_f 0.10 (6). Found, %: C 47.96; H 4.09; N 36.87. $C_6H_6N_4O$. Calculated, %: C 48.00; H 4.03; N 37.32. Mass spectrum, m/z: 150 $[M]^+$, IR spectrum in KBr (ν, cm^{-1}): 3200-2400 (NH, CH), 1635 (CO), 1620, 1597, 1570 (C=N, C=C). PMR spectrum in DMSO-d_6 (δ, ppm; J, Hz): 12.25 br. s (NH), 7.83 d (H^5, ^3J = 5.8), 5.95 d (H^6, ^3J = 5.8), 4.32 s (Me).

LITERATURE CITED

1. Z.-t. Huang and Z.-r Liu, Chem. Ber., 122, No. 1, 95 (1989).
2. V. Aggarwal, H. Ila, and H. Junjappa, Synthesis, No. 1, 65 (1982).
3. V. A. Dorokhov, M. F. Gordeev, A. V. Komkov, and V. S. Bogdanov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 401 (1990).
4. S. G. Alekseev, V. N. Charushin, O. N. Chupakhin, M. F. Gordeev, and V. A. Dorokhov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 494 (1989).
5. N. I. Viswanathan and V. Balakrishnan, J. Chem. Soc. Perkin Trans. 1, No. 10, 2361 (1979).
6. N. Grassivaro, E. Rossi, and R. Stradi, Synthesis, No. 12, 1010 (1986).
7. R. T. Chakrasali, H. Ila, and H. Junjappa, Synthesis, No. 11, 851 (1988).
8. A. Albert, Advanced Heterocyclic Chemistry, Vol. 39, Academic Press, New York (1986), p. 117.
9. Application for invention rights 81 131 587 Japan, Chem. Abstrs., 96, 122819 b (1982).
10. A. Albert and H. Taguchi, J. Chem. Soc. Perkin Trans. 2, No. 19, 2037 (1973).
11. T. Higashino, T. Katori, and S. Yoshida, Chem. Pharm. Bull., 27, No. 12, 3176 (1979).
12. T. Higashino, M. Takemoto, A. Miyashita, et al., Chem. Pharm. Bull., 33, No. 4, 1395 (1985).
13. H. Wamhoff, Comprehensive Heterocyclic Chemistry, Vol. 5, Pergamon Press, New York (1984), p. 669.
14. D. L. Rector and R. E. Harmon, J. Org. Chem., 31, No. 9, 2837 (1966).

OXIDATIVE DIMERIZATION OF HETEROCYCLIC NITRONES, DERIVATIVES OF PYRROLINE AND IMIDAZOLINE

V. A. Reznikov, V. V. Martin, and L. B. Volodarskii

UDC 542.943.7:547.743.4:
547.781.5

The oxidation of β-oxonitrones, derivatives of pyrroline and imidazoline, afforded symmetric dimers with a C–C bond and dehydrodimers with a C=C bond. Oxidation of the trifluoroacetyl imidazoline derivative afforded an asymmetric dimer. The oxidative dimerization of endocyclic β-oxonitrones, derivatives of pyrroline, proceeded much faster than that of exocyclic β-oxonitrones, derivatives of imidazoline. Imidazoline derivatives containing a perfluorophenyl or cyano group at the α-carbon atom on the nitrone group also underwent oxidative dimerization.

Oxidative dimerization, with formation of a carbon–carbon saturated bond or an ethylene bond [1, 2], is a characteristic reaction of alkyl nitrones (I) conttaining an electron-acceptor substituent in the β-position. Vinyl nitroxyl radical (II) is formed during the first stage of the reaction [3, 4]. Radicals (II), in which the spin density is distributed between nitroxyl and vinyl fragments [5], are relatively stable and may be observed by means of EPR [6]. In some cases the less stable C–O dimer (V) is formed [7] (see top of following page).

In continuing the study of heterocyclic nitrones, derivatives of pyrroline [8] and imidazoline [9], we examined their oxidative reactions in order to elucidate the characteristics of these reactions in a series of heterocyclic nitrones.

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1398-1404, June, 1990. Original article submitted April 24, 1989.

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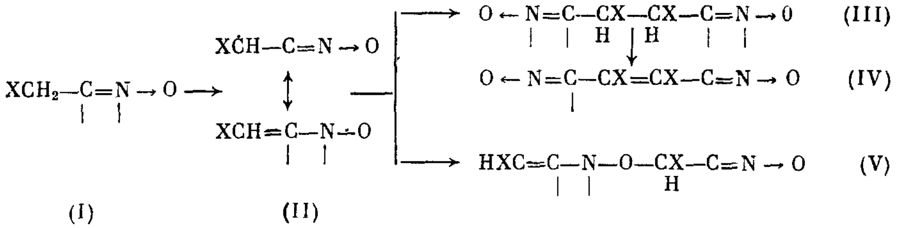
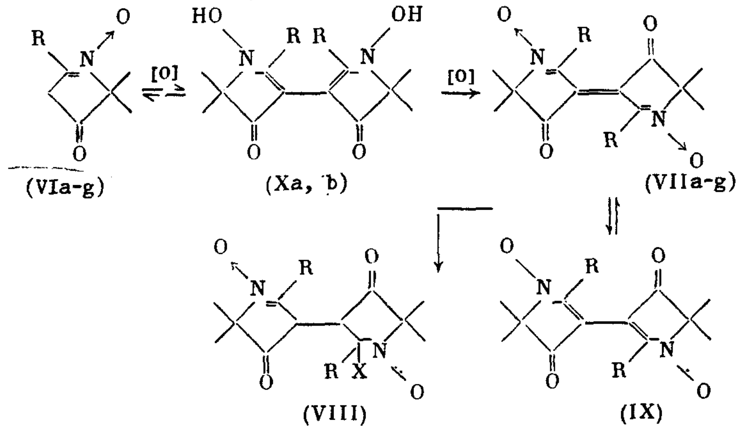


Pyrroline N-oxides (VI), containing a carbonyl group in the β-position with respect to the nitrone group, are very easily oxidized by atmospheric oxygen, Fe(III) salts, and manganese and lead dioxides. The reaction is complete after several minutes and affords ethylene-type dimers (VII), which are deeply colored compounds. This has been confirmed by mass spectral data, elemental analysis, and UV spectra, in which the absorption of conjugated nitrone groups is observed at 450-500 nm (Table 1). The PMR spectrum of compound (VIIa) (Table 2) contains proton signals of four methyl groups at 1.42 ppm and of two methyl groups at 2.36 ppm. The ^{13}C NMR spectrum contains signals of C=O carbon atoms (197.91 ppm), nitrone group (151.71 ppm), and ethylene bond carbon atoms (121.92 ppm). The presence of one set of hydrogen atom signals in the PMR spectrum and of carbon atom signals in the ^{13}C NMR spectrum indicates that compounds (VII) exist in a symmetric trans configuration relative to the C=C bond.

It should be noted that, because of their extraordinarily easy oxidative dimerization, pyrrolines (VIf, g) cannot be isolated in analytically pure form. The oxidation of these compounds continues during chromatography on silica gel.

It was unexpectedly observed that solutions of compounds (VIIc-g) emit a low-intensity EPR signal. This may be due to the fact that the nitrone group of compounds (VII) acts as a trap for short-lived radicals (X), and the EPR signal corresponds to spin adduct (VIII)* or to singlet–triplet transitions in compounds (VII), which produce biradicals (IX) in solution (cf. [11]). In the first case the EPR spectrum should consist of an equidistant triplet with the HFI constant $\alpha_N \approx 15$ Oe, which is characteristic of nitroxyl radicals (the HFI constant for vinyl nitroxyl radicals is almost two times smaller [6]). In the second case we may expect a quintet EPR spectrum with the HFI constant $\alpha_N \sim 8$ Oe, characteristic for the vinyl nitroxyl fragment [6]. A quintet EPR spectrum with $\alpha_N = 8.4$ Oe, showing the presence of biradical particles in solution, is observed for compound (VIId) solutions. The EPR spectrum of compound (VIIe) is a superposition of a quintet, with $\alpha_N = 8.8$ Oe, and a triplet, with $\alpha_N = 15.7$ Oe. The interpretation of the EPR spectrum of fluorine-containing compound (VIIc) is complicated by additional splitting on fluorine atoms. The EPR spectra of compounds (VIIc, f, g) are triplets with $\alpha_N = 15.3$ Oe, corresponding to nitroxyl monoradicals. Thus, it is likely that both pathways for the formation of nitroxyl radical centers are utilized for compounds (VII). The presence of paramagnetic particles in compound (VII) solutions causes line broadening in PMR spectra. Compound (VIIa), whose solution does not produce an EPR spectrum, is an exception.



R = CH_3 (a), C_6H_5 (b), CF_3 (c), $C(CH_3)_3$ (d), 2-pyridyl (e), CH_2Cl (f), $CO_2C_2H_5$ (g).

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*The appearance of an EPR spectrum for nitrones, which is caused by the formation of spin adducts with "extrinsic" radicals, is a very common phenomenon necessitating the use of special techniques for nitrone purification (see, for example, [12]).

TABLE 1. Characteristics of the Synthesized Compounds

Compound	Yield, %	mp,* °C	Found/Calculated, %			Formula †	IR spectrum (KBr), ν, cm^{-1}	UV spectrum (ethanol) λ_{max}, nm (log ε)
			C	H	N			
(VIIa)	90	160–162	60.3 60,4	6,6 6,5	9.9 10,1	$C_{14}H_{18}N_2O_4$	1730 (C=O), 1490 (C=C, C=N → O)	222(3,96), 278(3,85) 333(3,93), 498(4,27)
(VIIb)	90	228–229	71,4 71,6	5.7 5,5	6,8 7,0	$C_{24}H_{22}N_2O_4$	1725 (C=O). 1480, 1445, 1430 (C=C––C=N → O)	257(4,30), 355(3,94) 519(4,12)
(VIIc)	85	200–201	43,5 43,5	3,1 3,1	7,3 7,3	$C_{14}H_{12}F_6N_2O_4$	1740 (C=O), 1500 (C=C, C=N → O)	217(3,89), 271(3,88) 368(4,01), 444(4,12) 492(4,03)
(VIId)	80	127–129	66.6 66,3	8,6 8,3	7,7 7,7	$C_{20}H_{30}N_2O_4$	1720 (C=O), 1490 (C=C, C=N → O)	233(3,86), 304(3,97) 371(3,78), 567(4,03)
(VIIe)	90	207–209	65.3 65,5	5.0 5,0	13.5 13,8	$C_{22}H_{20}N_4O_4$	1720 (C=O). 1590 (C=N), 1480 (C=C–C=N → O)	230(4,21), 275(4.11) 320(3,7)
(VIIf)	45	173–174	48,6 48,5	4.7 4,6	7.9 8,1	$C_{14}H_{16}Cl_2N_2O_4$	1715 (C=O), 1480 (C=N → O)	228(3,99), 278(3,78) 350(3,92), 472(4,28)
(VIIg)	40	198–201	54.9 54,8	5.6 5,6	7,1 7,1	$C_{18}H_{22}N_2O_8$	1735 (C=O), 1630, 1590, 1500 (C=N, C=C)	349(4,11), 455(4,24)
(Xa)	30	275–277	59.6 60,0	6,9 7,1	9,7 10,0	$C_{14}H_{20}N_2O_4$	band width . . 1410–1560, 1600–1660 (N–C=C–C=O)	226(3,83), 283(4,03) 335(3,86), 500(3,82)
(Xb)	80	>360	71.3 71,3	6.2 5,9	7,0 7,0	$C_{24}H_{24}N_2O_4$	1610. 1640, 1670 (C=O, C=C)	247(4,16), 352(3,48) 520(3,0)
(XIII)	71	167–169	66.3 65,9	6.5 6,3	9.9 10,3	$C_{30}H_{34}N_4O_6$	1580 (C=N), 1675 (C=O)	228(4,10), 272(4,12)
(XIVa)	70	153–155	70,3 70,3	8,0 7,7	10.2 10,2	$C_{32}H_{42}N_4O_4$	1685 (C=O). 1600 (C=C), 1570, 1580 (C=N → O)	250(4,23)
(XIVb)	60	182–184	66.7 66,6	10,1 9,9	11.1 11,1	$C_{28}H_{50}N_4O_4$	1705 (C=O), 1575 (C=N)	252(3,75)
(XV)	62	65–68	53.9 53,6	5,0 5,1	8,6 8,3	$C_{15}H_{17}N_2F_5O$	1620 (C=N)	235(4,01)
(XVI)	90	93–95	53,5 53,9	4,4 4,5	8,6 8,4	$C_{30}H_{30}N_4F_{10}O_2$	1550 (C=N)	250(3,83), 318(4,09)
(XVII)	70	193–195	61.9 62,2	8,0 7,8	21,5 21,8	$C_{20}H_{30}N_6O_2$	1520, 1540 (C=C, C=N), 2230 (C≡N)	277(4,02), 416(3,98) 480(3,62)
(XX)	48	185–187	54.9 54,7	4,2 4,1	10.6 10,6	$C_{18}H_{16}N_3F_3O_4$	1720 (C=O), 1590 (C=N)	253(4,07), 367(3,96) 483(4,16)
(XXII)	94	215–218	49.3 49.6	6.7 6.4	10,5 10.2	$C_{22}H_{34}N_4F_6O_4$	1580 (C=N), 1640 (C=C)	238(4,12), 285(3,81)

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*Compounds (VIIa-f), (X), (XIII), and (XX) were purified chromatographically; compounds (VIIg), (XVI), and (XVII) were recrystallized from ethyl acetate–hexane; compound (XIV), from aqueous alcohol; (XV), from pentane; (XXII), from ethyl acetate.

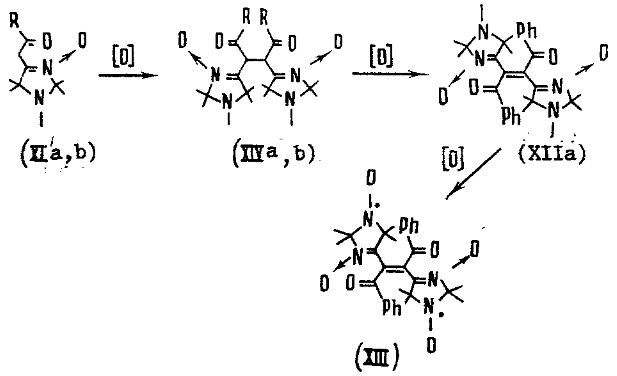
†Found/Calculated, % (F): 29.8/29.6 (VIIc), 27.8/28.3 (XV), 29.0/28.4 (XVI), 14.4/14.4 (XX), 21.9/21.4 (XXII). Found/Calculated, % (Cl): 20.3/20.5 (VIIf).

TABLE 2. PMR Spectra of the Synthesized Compounds

Compound	δ, ppm ($CDCl_3$, s)
(VIIa)	1,42 (6H, 5,5-$(CH_3)_2$), 2,36 (3H, 2-CH_3)
(XIVa)	1,05 (6H), 1,18 (3H), 1,26 (3H) (2,5-$(CH_3)_2$), 2,15 (3H, N-CH_3), 7,6 m (5H, C_6H_5)
(XV)	1,21 (6H), 1,44 (6H) (2,5-$(CH_3)_2$), 2,37 (3H, N-CH_3), 3,81 (2H, -CH_2-)
(XVI)	1,46 (6H), 1,48 (6H) (2,5-$(CH_3)_2$), 2,34 (3H, N-CH_3)
(XVII)	1,41 (6H), 1,44 (6H), 1,56 (6H), 1,74 (6H) (2,5-$(CH_3)_2$ and 2′,5′-$(CH_3)_2$), 2,34 (3H, N-CH_3)
(XXII)	1,24 (6H), 1,38 (12H), 1,47 (6H) (2,5-$(CH_3)_2$ and 2′,5′-$(CH_3)_2$), 2,20 (3H, N-CH_3), 2,33 (3H, N-CH_3), 4,03 (2H, J_{AB}=15 Hz, -CH_2-), 10,61 (1H), 11,35 (1H, OH)

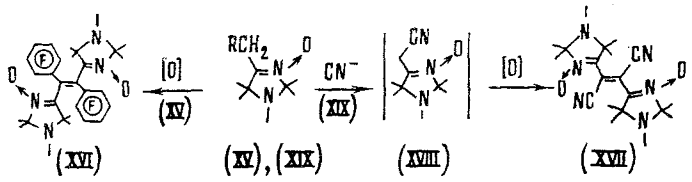
When compound (VIa, b) solutions are heated or the compounds are kept over a prolonged period of time in solid form at room temperature, compounds (Xa, b) are formed. When chromatographed or kept in solution, these compounds afford a mixture of the original pyrrolines (VIa, b) and ethylene dimers (VIIa, b). In the presence of manganese or lead dioxides, compounds (Xa, b) are converted quantitatively to pyrroline dimers (VIIa, b). On the basis of these data as well as elemental analysis, these compounds were assigned the structures (Xa, b). The ^{13}C NMR spectra of compounds (Xa, b) in DMSO are very similar to those of pyrrolines (VIa, b). Compounds (Xa, b) exist in tautomeric form with the enolized nitrone group (cf. [8]). Compound (Xb) has a double set of signals, which may be caused by an asymmetric configuration relative to the C_3—C_3' bond, due to the bulky phenyl groups, so that the heterocyclic fragments become nonequivalent.

Phenacyl nitrone, a derivative of 3-imidazoline 3-oxide (XIa), is oxidized by manganese and lead dioxides to ethylene dimer (XIIa) [9], which undergoes oxidative dealkylation to form biradical (XIII). It should be noted that the oxidation of compound (XIa) is much lower than that of pyrroline derivatives; when the compound is oxidized by manganese dioxide, intermediate product (XIVa), with a single C—C bond, can be isolated. Unlike pyrroline dimers (IX), compound (XIVa) exists in the unenolized form, as indicated by its spectral characteristics. Thus, the IR spectrum of compound (XIVa) contains a band at 1685 cm^{-1} ($C_6H_5-\underset{|}{C}=O$), and the UV spectrum contains an absorption band at 250 nm, corresponding to an unconjugated nitrone group; the PMR spectrum contains a proton signal at 5.92 ppm. Further oxidation of compound (XIVa) readily affords dimer (XIIa). By contrast, the oxidation of pivaloyl nitrone (XIb) affords only dimer (XIVb), which is resistant to oxidizing agents.



R = C_6H_5 (a), $C(CH_3)_3$ (b).

Attempts at oxidative dimerization, by manganese and lead dioxides, of type (XV) imidazoline derivatives, in which R is an alkyl substituent, halogen atom, or azido group [13], were unsuccessful; the original compounds were regenerated quantitatively from the reaction mixture. On the other hand, oxidation of pentafluorobenzyl nitrone (XV) by lead dioxide readily afforded dimer (XVI). For the reaction to proceed, the R substituent should exhibit a negative mesomeric effect. The cyano group exhibits such an effect; therefore, dehydrodimer (XVII) was the only product isolated in an attempt to synthesize cyanomethyl nitrone (XVIII) by nucleophilic substitution of bromine in 4-bromomethyl-1,2,2,5,5-pentamethyl-3-imidazoline-3-oxide-1-oxyl (XIX).

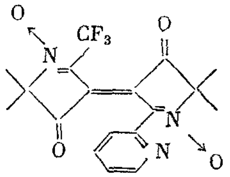


R = C_6F_5 (XV), Br (XIX).

In general, pyrroline derivatives (VI) are oxidized much more rapidly than imidazoline derivatives (XI). This may be due to the fact that compounds (VI) exist in the N-hydroxyl form [8], in which the removal of a hydrogen atom during oxidation is facilitated [4], whereas in β-oxonitrones enolization occurs primarily at the carbonyl group, and removal of a hydrogen atom is impeded by a strong intramolecular hydrogen bond [9, 10]. In nitrones without substituents exhibiting a mesomeric effect the tautomeric equilibrium is shifted completely toward the nitrone form.

The different oxidation rates of pyrroline and imidazoline derivatives may be the reason that no "mixed" dimers are observed in the reaction mixture during joint oxidation of pyrroline [for example, (VIb) or (VIe)] and imidazoline [(XIa) or (XIb)] derivatives; the reaction products are pyrroline (VII) and imidazoline (XII) dimers. Joint oxidation of pyrroline derivatives (VIc) and (VIe), on the other hand, affords a mixture of dimers (VIIc) and (VIIe) and the mixed dimer (XX) in a nearly statistical ratio (1:1:2).

(VIc) + (VIe) → (VIIc) + (VIIe) +



(XX)

Under oxidative dimerization conditions, trifluoroacetyl nitrone (XXI) forms a single product (XXII), whose molecular weight is consistent with a dimer. However, the spectral characteristics of this compound differ significantly from those of dimers (XXII) and (XIV). Thus, the IR spectrum of compound (XXII) lacks a carbonyl group absorption band and contains an intramolecular hydrogen bond absorption band. The PMR spectrum contains signals of two nonequivalent N-methyl groups, showing that the heterocyclic fragments are nonequivalent, as well as methylene proton signals at 4.03 ppm. On the basis of these data compound (XXII) was assigned a dimer structure in which a C–C bond is formed between the nitrone and carbonyl carbon atoms. The free β-oxonitrone fragment is enolized either at the carbonyl or nitrone groups (cf. [9]).

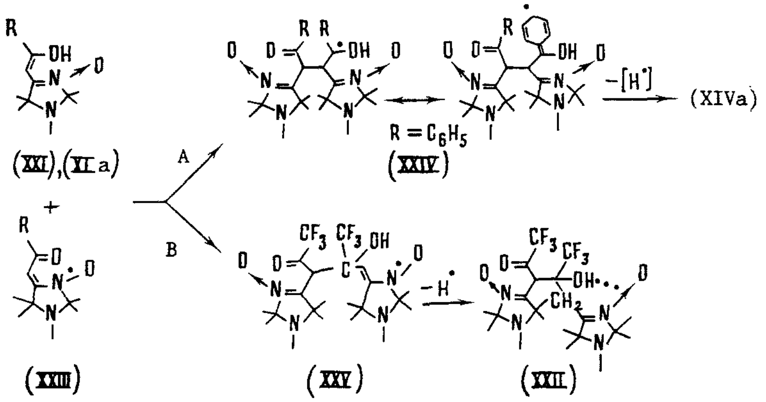
The formation of compound (XXII) can be understood if we assume that intermediate vinyl nitroxyl radical (XXIII) can react with another molecule of the original compound (represented in the enol form) either by pathway A or pathway B. The first pathway produces an ethane dimer, and the second affords a type (XXII) compound. The factors determining the direction of the reaction are as yet unclear, though we might expect that substituents that stabilize intermediate radical (XXIV) would direct the reaction along pathway A, while less stabilizing substituents would direct the reaction along pathway B, in which intermediate radical (XXV) is stabilized by the nitroxyl structure (see top of following page).

The authors express their gratitude to V. N. Parmon for a discussion of the results.

EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument in KBr (concentration, 0.25%); UV spectra were recorded on a Specord UV-VIS instrument in ethanol. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 instrument pulsed for 10-15% solutions in $CDCl_3$ and DMSO-d_6. The EPR spectra were recorded on a Bruker EP-200 SRC spectrometer for 10^{-2} M solutions in acetone. Mass spectra were recorded on a Finnigan MAT 8200 instrument.

Oxidation of Pyrrolines (VI) (General Method). A solution of 0.2 g pyrroline (VI) in 20 ml dry ether was mixed with 1 g MnO_2 for 5 min. The excess oxidant was filtered off, and the filtrate was evaporated. Compound (VII) was isolated by chromatography on a silica gel column, with ethyl acetate–hexane (1:2) as eluent. The following compounds were obtained:



R = C_6H_5 (XIa), CF_3 (XXI).

2-methyl- (VIIa), 2-phenyl- (VIIb), 2-trifluoromethyl- (VIIc), 2-(2-pyridyl)- (VIIe), 2-tert-butyl-bis(5,5-dimethyl-1-oxide-4-oxopyrrolin-1-ylidene-3) (VIId). Bis-(5,5-dimethyl-1-oxide-4-oxo-2-chloromethylpyrrolin-1-ylidene-3) (VIIf) and bis(5,5-dimethyl-1-oxide-4-oxo-2-ethoxycarbonylpyrrolin-1-ylidene-3) (VIIg) were obtained by oxidation of unpurified pyrrolines (VIf, g), synthesized according to [8]. Similarly, joint oxidation of pyrrolines (VIc) and (VIe) afforded 3-(5,5-dimethyl-4-oxo-2-trifluoromethylpyrroline-1-oxide-1-ylidene-3)-5,5-dimethyl-4-oxo-(2-pyridyl)-1-pyrroline-1-oxide (XX). ^{13}C NMR spectrum of compound (VIIa) in $CDCl_3$ (δ, ppm): 13.26 ($2-CH_3$), 20.86 ($5-(CH_3)_2$), 72.48 (C^5), 121.92 (C^3), 197.91 (C^4).

^{13}C NMR spectrum of compound (VIIb) in $CDCl_3$ (δ, ppm): 14.15 ($5-(CH_3)_2$), 66.26 (C^5), 113.52 (C^3), 120.50, 120.67, 122.55, 123.60 (o-, m-, p-, i-C_6H_5), 142.36 (C^2), 187.86 (C^4).

Mass spectrum (M^+, found/calculated): 278/278 (VIIa), 402/402 (VIIb), 386/386 (VIIc), 362/362 (VIId), 394/394 (VIIf).

Bis(1-hydroxy-4-oxo-2,5,5-trimethylpyrrolin-2-yl-3) (Xa). A solution containing 0.2 g pyrroline (VIa) in 5 ml toluene, morpholine, or triethyl phosphate was heated for 15 min at 100-120°C and dissolved in 10 ml ether. The compound (Xa) residue was filtered, washed with ether, and dried. Similarly, heating of pyrroline (VIb) afforded bis(1-hydroxy-4-oxo-5,5-dimethyl-2-phenylpyrrolin-2-yl-3) (Xb).

^{13}C NMR spectrum of compound (Xa) in DMSO-d_6 (δ, ppm): 13.15 ($2-CH_3$), 21.48 ($5-(CH_3)_2$), 69.31 (C^5), 100.64 (C^3), 174.53 (C^2), 197.52 (C^4).

^{13}C NMR spectrum of compound (Xb) in DMSO-d_6 (δ, ppm): 21.33, 22.46, 23.15, 24.09 ($5,5-(CH_3)_2$), 62.65, 69.86 (C^5), 97.59, 105.81 (C^3), 126.95, 127.48, 127.69, 128.24, 128.45, 129.75, 130.66, 130.94, 131.73 (C_6H_5), 170.34, 173.91 (C^2), 200.60, 202.16 (C^4).

1,4-Dioxo-2,3-bis(3-oxide-1,2,2,5,5-pentamethyl-3-imidazolin-4-yl)-1,4-diphenylbutane (XIVa). A solution of 0.5 g imidazoline (XIa) in 20 ml chloroform was mixed with 2 g MnO_2 or PbO_2 for 1 h. The excess oxidant was filtered off, the solution was evaporated, and the residue was ground with hexane. Precipitate (XIVa) was filtered off. When the mixing time was increased to 10 h, the reaction product was ethylene dimer (XII) [9]. Oxidation of pivaloyl nitrone (XIb) under the same conditions afforded 1,4-dioxo-2,3-bis(3-oxide-1,2,2,5,5-pentamethyl-3-imidazolin-4-yl)-1,4-ditert-butylbutane (XIVb). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm): 22.47, 23.84, 24.28, 25.95 ($2.5-(CH_3)_2$), 26.12 ($N-CH_3$), 44.41 ($CO-\underline{C}(CH_3)-C$), 25.95, 45.41 ($C(CH_3)_3$), 64.56 (C^5), 88.50 (C^2), 139.74 (C^4), 211.82 ($C{=}O$). The oxidation of pentafluorophenyl nitrone (XV), obtained from the reaction of metallized imidazoline with hexafluorobenzene according to [9], under the same conditions afforded 1,2-bis(1,2,2,5,5-pentamethyl-3-imidazoline-3-oxid-4-yl)-1,2-bis(pentafluorophenyl)ethylene (XVI). Similarly, oxidation of trifluoroacetyl derivative (XXI) afforded 4-hydroxy-3,5-bis(1,2,2,5,5-pentamethyl-3-imidazoline-1-oxid-4-yl)- 2-oxo-1,1,1-trifluoro-4-trifluoromethylpentane (XXII).

The oxidation of compounds (XIa, b) and (XV) by atmospheric oxygen in the presence of copper ammoniate according to [8] afforded compounds (XII), (XIVa), and (XVI). The molecular mass found (boiling point method) for compound (XVI) was 680; the calculated mass was 668. Trifluoroacetyl derivative (XXI) was oxidized with MnO_2 or PbO_2 as described above.

1,2-Bis(1,2,2,5,5-pentamethyl-3-imidazoline-3-oxid-4-yl)-1,2-dicyanoethylene (XXVII). A solution of 3.31 g bromo derivative (XIX), 1.3 g KCN, and 20 mg 18-crown-6-ether in 100 ml acetonitrile was mixed for 50 h, filtered, and evaporated. Compound (XXVII) was isolated by chromatography on a silica gel column (eluent, $CHCl_3$).

Biradical (XIII) was synthesized by oxidative dealkylation of compound (XII) according to [9].

LITERATURE CITED

1. E. Brewer, in: The Chemistry of Functional Groups, Supplement F, S. Patai (ed.), Interscience, Chichester (1982), Part 1, p. 459.
2. D. St. C. Black, V. M. Clark, B. G. Odell, and Todd Lord, J. Chem. Soc. Perkin Trans. 1, 1944 (1976).
3. H. G. Aurich, Can. J. Chem., 60, 1414 (1982).
4. H. G. Aurich, M. Schmidt, and Th. Schwerzel, Chem. Ber., 118, 1105 (1985).
5. H. G. Aurich, K. Hahn, and K. Stork, Chem. Ber., 112, 2776 (1979).
6. H. G. Aurich, M. Schmidt, and Th. Schwerzel, Chem. Ber., 118, 1086 (1985).
7. H. G. Aurich, International Conference on Nitroxide Radicals, Novosibirsk (1989), p. 13.
8. V. A. Reznikov and L. B. Volodarskii, Khim. Geterotsikl. Soedin., No. 12, 1661 (1989).
9. V. V. Martin and L. B. Volodarskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1336 (1980).
10. V. A. Reznikov and L. B. Volodarskii, Khim. Geterotsikl. Soedin., No. 1, 103 (1990).
11. V. N. Parmon, A. I. Kokorin, and G. M. Zhidomirov, Stable Biradicals [in Russian], Nauka, Moscow (1980).
12. V. E. Zubarev, The Spin Trap Method: Its Applications in Chemistry, Biology, and Medicine [in Russian], Izd. Mosk. Gos. Univ., Moscow (1985).
13. I. A. Grigor'ev, V. V. Martin, G. I. Shchukin, and L. B. Volodarskii, Izv. Akad. Nauk SSSR, Ser. Khim., 2711 (1979).