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Synthesis and Structure of Products of Hydroxylamine Acylation with 3-Carboxy-2,2,5,5-tetramethylpyrrolinoxyl Derivatives

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Abstract—The reaction of NH_2OH with the derivatives of 2,2,5,5-tetramethylpyrrolin-1-oxyl-3-carboxylic acid in all events led to the formation of a mixture of the corresponding nitroxylhydroxamic acid with a stable O-acylhydroxylamine. The ratio between the products depends on the nature of the acylating agent and under the studied conditions varies from ~5.5 : 1 to 1 : 3 indicating the comparable nucleophilicity in this reaction of N and O atoms in the hydroxylamine. The most active chloride of the mentioned acid alongside the indicated products afforded in a considerable yield N,O-diacylhydroxylamine and the triacylated hydroxylamine, 3-{[(2,2,5,5-tetramethyl-1-oxylopyrrolin-3-yl)carbonyloxyimino][(2,2,5,5-tetramethyl-1-oxylopyrrolin-3-yl)carbonyloxy]-methyl}-2,2,5,5-tetramethylpyrrolin-1-oxyl. The structure of both latter compounds was established by XRD analysis.

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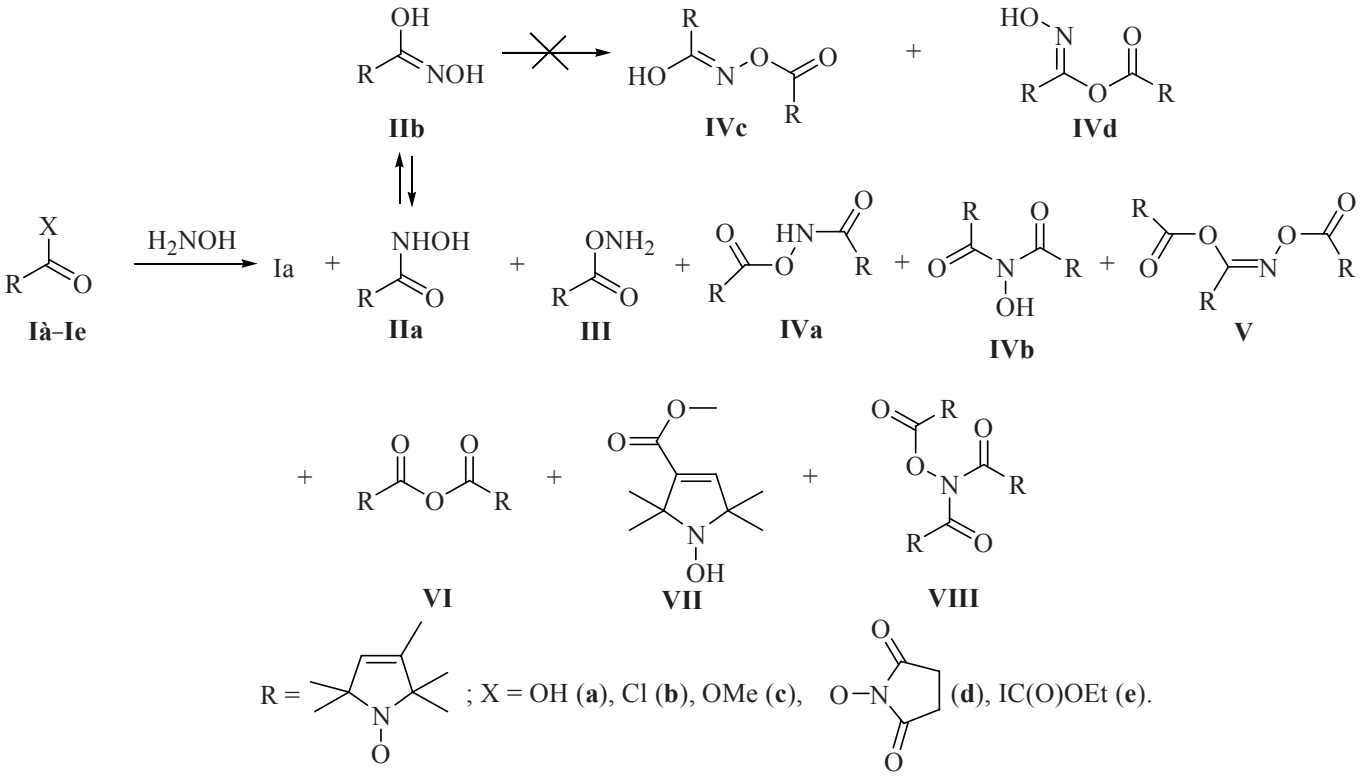
In the preceding study [1] we developed a preparation procedure for nitroxylhydroxamic acids that might potentially combine the wide range of biological action of hydroxamic acids [2] and nitroxyl radicals [3] and besides were interesting as a research tool at the use of ESR method. In the developed method the carboxy group was activated by converting it into acid chloride. Inasmuch as it was possible to obtain acid chlorides only for a few five- and six-membered cyclic nitroxylcarboxylic acids, procedure [1] was of limited applicability. The other known methods of hydroxamic acids synthesis are N-acylations of hydroxylamine or its O-protected derivatives with carboxylic acids esters and with mixed anhydrides with carbonic acid esters [4]. The O-protected derivatives of hydroxylamine are hardly suitable for the synthesis of nitroxylhydroxamic acids because the nitroxyl radicals are unstable under the conditions of acid hydrolysis [5] or hydrogenolysis [6] of the protective groups. In the first case the nitroxyl radicals suffer acid disproportionation [7], and in the second event they are reduced to hydroxylamines [8]. The disadvantage of the acylation of unprotected hydroxylamine consists in the formation of a mixture of products of mono-, di-, and triacylation. To our knowledge no systematic studies were performed concerning the effect of carboxylic acids activation on the selectivity of NH_2OH acylation [9–11]. The di- and triacyl derivatives of NH_2OH, have their proper interest, for they may be present as isomers. Isomers of di- and triacyl derivatives of NH_2OH may form at alternative N-/O-acylation of NH_2OH monoacyl derivatives, and also due to the hydroxame-hydroxime tautomerism in the hydroxamic acids and their derivatives. By few examples of NH_2OH N,O-diacyl derivatives it was shown [12–15] that unambiguous proof of their structure could be obtained only by XRD method.

In this study we investigated in detail the reaction of the hydroxylamine with derivatives of the most available nitroxylcarboxylic acid, 3-carboxy-2,2,5,5-tetramethylpyrrolin-1-oxyl (**Ia**): its acid chloride **Ib**, methyl ester **Ic**, *N*-hydroxysuccinimide ester **Id**, mixed anhydride **Ie**, and also we performed the condensation of acid **Ia** with NH_2OH using dicyclohexylcarbodiimide (DCC). The effect of the method of acid **Ia** activation on the yield of reaction products was evaluated. The structures of products were established from spectral data and by XRD analysis.

The reaction products obtained from NH_2OH with



acid **Ia** and its derivatives and the products yields are presented on the scheme and in Table 1.

An important feature of reactions between compounds **Ia–Ie** and NH_2OH is the obligatory formation of the mixture of products of N- and O-acylation, hydroxamic acid **IIa** and O-acylhydroxylamine **III** respectively. Compound **III** is stable and unlike the majority of known examples [9] does not undergo isomerization when treated with excess NH_2OH into the more thermodynamically feasible hydroxamic acid **IIa**. The ratio between the yields of compounds **IIa** and **III** depends on the nature of the acylating agent and varies under the studied conditions from ~5.5:1 to 1:3 (Table 1) indicating the comparable nucleophilicity in this reaction of N and O atoms in the hydroxylamine. One more reaction proceeds simultaneously: reduction with hydroxylamine of nitroxyl groups of radicals **Ia–Ie**. This reaction was relatively slow, and the reduction product **VII** was identified only in the case of a weak acylating agent, methyl ester **Ic**. At the use of active acylating agents **Ib, Id**, and **Ie** or of the system **Ia**–DCC and slight excess of NH_2OH the products of the nitroxyl group reduction were not formed in considerable amounts.

Pyrrolinecarboxylic acid **Ia** with DCC and acid chloride

Table 1. Yields of products of reaction of acid **Ia** and its derivatives with NH_2OH

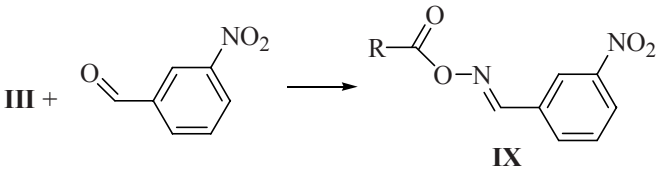
No. of initial compound	Solvent – base	Yield of reaction product, %[a]						
		Ia	**IIa**	**III**	**IVa**	**V**	**VI**	**VII**
Ia	MeCN	–	70 (39)	25	–	–	–	–
Ib	MeCN–Et_3N	–	67 (54)	12	15	–	–	–
Ib	MeCN–Py	–	10	13	42 (7)	26 (2)	1	–
Ic	EtOH	–	3	1	–	–	–	60
Id	MeOH	–	23	75 (71)	2	–	–	–
Ie	C_6H_6	10	20	68	1	–	–	–
	MeCN	12	42	42	4	–	–	–

[a] Found by HPLC with respect to the initial compound; preparative yield is given in parentheses.

Ib with Et_3N acylated NH_2OH predominantly at the nitrogen atom and therefore they are the most efficient for the preparative synthesis of hydroxamic acid **IIa**. In contrast, the prevailing reaction with activated ester **Id** was O-acylation of hydroxylamine, and therefore this procedure is the most suitable for preparation of compound **III**. Hydroxylamine attached both carbonyl groups of the mixed anhydride **Ie** providing a difficultly separable mixture of compounds **Ia, IIa**, and **III**. Therefore reagent **Ie** is unsuitable for preparative procedures. Besides compounds **Ib** and **Ie** partially acylate the primarily formed compounds **IIa** and **III** to diacyl derivatives **IV** thus additionally complicating the separation of products. The employing of the most active acylating mixture of acid chloride **Ib** with pyridine resulted in the formation of all possible acylation products of NH_2OH.

In order to establish the formation routes of di- and triacyl derivatives of NH_2OH and also to understand the formation of anhydride **VI** in the process we investigated the reactions of acid **IIa**, ester **III**, and N,O-diacylhydroxylamine **IVa** with acid chloride **Ib**. In reaction of compound **IIa** with an equimolar quantity of acid chloride **Ib** in the presence of Et_3N formed biradical **IVa** in ~90% yield (by HPLC data). Another product of this reaction (yield ~5%) was also a biracial that was not preparatively isolated. The ESR spectrum of the latter radical in benzene (~10^{-4} mol l^{-1}) contains five lines with the amplitudes ratio 100:19:121:17:90 and splitting constant a_N 1.47 mT. This spectrum is characteristic of nitroxyl biradicals where the energy of exchange interaction J and a_N value are related by an expression $J \approx 10a_N$ [16]. The UV spectrum of this biradical in the eluent B (see EXPERIMENTAL) contains a single symmetric band with λ_{max} 217 nm characteristic of RC(O)-derivatives of NH_2OH lacking C=N bond (see below). These data are consistent with the structure of biradical **IVb** and disagree with the structures of the hydroximic acid derivatives **IVc** and **IVd**. Hence under the conditions we studied hydroxamic acid **IIa** underwent both O- and N-acylation with the rates ratio ~20 : 1 respectively. The presumable hydroximic tautomer **IIb** was not detected in the solution by IR spectroscopy and did not notably yield its acylation products **IVc** and **IVd**.

The expectable main product in the reaction of ester **III** with acid chloride **Ib** would be derivative **IVa**. However the HPLC data showed that at equimolar reagents ratio in the presence of Et_3N anhydride **VI** was obtained in 92% yield, and the yield of the expected compound **IVa** was only 1%. The reaction was carried out under anhydrous conditions. and the only possible way to understand the high yield of anhydride **VI** was to assume a formal O-acylation of ester **III** along an unclear mechanism. When the base used in the reaction was $NaHCO_3$ the N-acylation of compound **III** prevailed, and the ratio of yields of compounds **IVa** and **VI** was 5:1. In the acylation of ester **III** with mixed anhydride **Ie** compound **IVa** also formed as the main product, the ratio of yields of compounds **IVa** and **VI** was 19:1.



IX

The structure of hydroxylamine O-ester **III** was also confirmed by its reaction with *m*-nitrobenzaldehyde that afforded in 93%-νьμ yield the expected azomethine **IX**.

Triradical **V** formed in a high yield both in the reaction of acid **IIa** with a double quantity of acid chloride **Ib** and in the reaction of biradical **IVa** with an equimolar amount of compound **Ib** (yields 91 and 83% respectively). In both cases in an yield ~7% another isomer of triradical was obtained whose ESR spectrum in eluent B contained 7 lines with the amplitudes ratio 100 : 79 : 89 : 132 : 126 : 63 : 89 and a splitting constant a_N 1.55 mT. This spectrum is characteristic of nitroxyl triradicals where the exchange interaction of unpaired electrons with the nitrogen nuclei is modulated by the intramolecular motion of the atoms [17]. The UV spectrum of this triradical in the eluent contains a single absorption band with λ_{max} 224 nm. It is presumable proceeding from the spectral data that the minor product of these reactions is either one of the eight possible stereoisomers of triradical **VIII** or one of sixteen possible steric isomers of triradical **V**.

The structure of acid **IIa** was established in the preceding communication [1]. The new pyrrolinoyl hydroxylamine derivatives **III, IVa**, and **V** are high-melting crystalline substances of yellow color. Their structure was established from elemental analysis, IK, ESR, UV, and mass spectra, and compounds **IVa** and **V** were besides subjected to XRD analysis.

IR spectrum of the chloroform solution of compound **III** contains an absorption band of an endocyclic C=C bond at 1629 cm^{-1} and bands characteristic of hydroxylamine O-acyl derivatives, 1729 cm^{-1} of the stretching vibrations of C=O group, 1553 cm^{-1} of the bending

vibrations of NH_2, 3229 and 3319 cm^{-1} of the symmetric and asymmetric vibrations of NH_2 [9, 18]. The carbonyl groups in the N- and O-acylhydroxylamines are known [9–11] to have absorption in different range of the IR spectrum providing a reliable tool for distinguishing these compounds. In *N*-acylhydroxylamines this amide band appears at 1640–1670 cm^{-1} (for acid **IIa** 1663 cm^{-1}) and in O-acylhydroxylamines the carbonyl is a part of the ester group and its absorption band is observed at 1720–1760 cm^{-1} (for compound **III** 1722 and 1729 cm^{-1} in solid state and in solution respectively).

Taking in consideration the existence in the solution of a tautomeric equilibrium between **IIa** and **IIb**, the acylation of the primarily formed mixture of compounds **IIa**, **IIb**, and **III** might provide four isomers of NH_2OH diacyl derivatives of structures represented by formulas **IVa–IVd**. The IR spectrum of the solution of isolated isomer **IV** in $CHCl_3$ contained the stretching vibrations bands at 1629 (C=C), 1705 (O=CN), 1769 (O=CO), and 3200 (N–H) cm^{-1}. Three latter bands are characteristic of the N,O-diacyl hydroxylamine derivatives [10, 14]; they are consistent with structure **IVa** and disagree with structures of isomers **IVb–IVd**. The triacyl derivatives may exist as isomers **V** and **VIII** whose benzoyl analogs have been described in [19, 20] like β- and α-isomers of tri-benzoylhydroxylamine respectively. The IR spectrum of the solution of isolated isomer of triradical in $CHCl_3$ contains the stretching vibrations bands at 1602 (C=N), 1631 (C=C), and 1760 (O=CO) cm^{-1} in agreement with structure **V**.

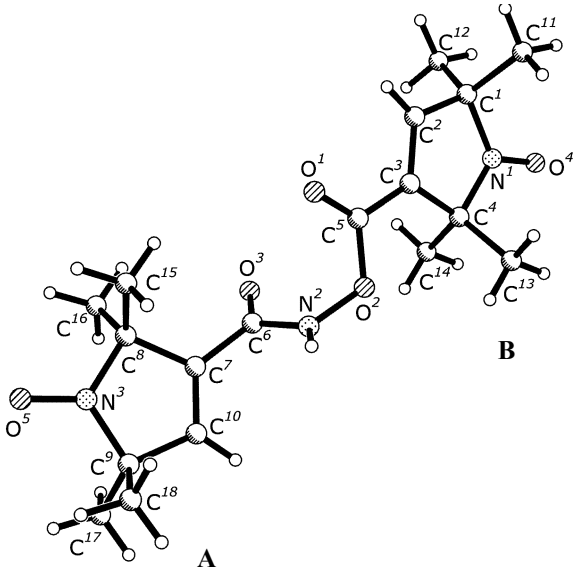


Fig. 1. Molecular structure of biradical **IVa**.

UV spectra of compounds **III** and **IVa** in the region 200–350 nm contain a single band with λ_{max} 208–216 nm. The molar extinction factor in this band for monoradical **III** is $\varepsilon \sim 10^4$ l mol^{-1} cm^{-1}, and for biradical **IVa** it is twice larger. In the spectrum of triradical **V** the absorption maximum is shifted to the longwave region (λ_{max} 223 nm) compared to the spectra of compounds **III** and **IVa**. This shift is evidently due to the overlapping of the absorption by the fragments C=C–C=N and C=C–C=O. The absorption band of the C=C–C=O group in compounds **III, IVa**, and **V** shields the weaker $\pi > \pi^*$ band of the nitroxyl group. The latter is observed as a shoulder at 244 nm in the spectrum of compound **V**. The yellow color of compounds obtained originates from the weak $\pi > \pi^*$ absorption of the nitroxyl group (~400 nm), $\varepsilon \sim 5$ l mol^{-1} cm^{-1} [21].

The ESR spectra of the dilute solutions of compound **III** contain three lines each due to the splitting on ^{14}N. In water solution at ~20°C the constant a_N is 1.63 mT, the value characteristic of the nitroxyl radical of pyrroline series [16]. The ESR spectrum of the dilute solution of **IVa** in benzene at ~20°C is composed of 9 lines with the amplitudes ratio (38 : 100 : 75) : (37 : 88 : 30) : (71 : 92 : 27), a_N 1.42 mT. This spectrum is consistent with the theoretical spectrum of nitroxyl biradicals with $J/a_N \approx 0.2$ [16]. The spectrum of triradical **V** in a benzene solution at ~20°C contains 7 lines with the amplitudes ratio 49 : 63 : 68 : 100 : 58 : 55 : 45 and is characheristic of nitroxyl triradicals [16]. The amplitudes ratio is different from the theoretical 1 : 3 : 6 : 7 : 6 : 3 : 1 for triradicals with $J \gg a_N$ because of broadening of all spectral lines save the extreme ones due to the modulation of the exchange interaction of three unpaired electrons by the intramolecular motions of atoms [17].

In mass spectra of compounds **III, IVa**, and **V** peaks of negative ions $[M - H]^-$ are observed whose masses correspond to the calculated values. In the spectra of all compounds strong peaks of fragment ions are present with *m*/*z* 168 and 183 originating from the splitting of CH_3 and N=O from $[C_9H_{14}N_2O_3]^-$. The mass spectra of compounds **III** and **IIa** [1] differ only in the intensity ratio of peaks $[M - H]^-$ and fragment ions.

The reported spectral data of compounds **IVa** and **V** completely correspond to the results of their XRD investigation (Figs. 1, 2). For N,O-diacylhydroxylamine **IVa** four *s-cis-trans*-isomers are possible. The bond lengths and bond angles in the obtained isomer **IVa** are compiled in Tables 2, 3. In this isomer the carbonyl group

and C=C bond in the N-acyl **A** are located in the *s-trans*-position, and in the O-acyl **B**, in *s-cis*-position with respect to each other. Both pyrroline rings **A** and **B** are planar, and the angle between the planes is 156.5°. The structures of the pyrroline ring in hydroxamic acid **IIa** [1] and **A** ring of molecule **IVa** differ insignificantly. The comparison in pairs of the bond lengths of double bonds C^7–C^{10} and C^2–C^3, and also of ordinary bonds C^7–C^8 and C^3–C^4 in **A** and **B** rings shows that the corresponding bonds in **B** ring are longer by ~0.03 Å. The lengths of the other bonds differ insignificantly. The longer endocyclic double bond in **B** ring suggests a stronger conjugation in the *s-cis*-fragment $O^1C^5C^3C^2$ of the O-acyl as compared to the *s-trans*-fragment $O^3C^6C^7C^{10}$ of the N-acyl. Besides the bond C^3–C^5 in the O-acyl is shorter than the bond C^6–C^7 in the N-acyl owing to the stronger conjugation. In agreement with the above stated the dihedral angle $O^3C^6C^7C^{10}$ in the N-acyl equals 57.2°, whereas the dihedral angle $O^1C^5C^3C^2$ in the O-acyl is only 3.7°. Dihedral angles $O^3C^6N^2O^2$ (0.1°), $C^6N^2O^2C^5$ (74.9°), and $N^2O^2C^5O^1$ (169.8°) are close to the values published for the other N,O-diacyl hydroxylamine derivatives [12, 14, 15]. For the dihedral angle $C^6N^2O^2C^5$ of N,O-dibenzoylhydroxylamine in solution the estimated value was 70° [22]. This fact indicates the sufficiently rigid conformation of this fragment and its weak deformation under the effect of the intermolecular forces in the crystal. The fragment $O^2C^5O^1C^3$ is flat and is turned relative to the plane $C^7C^6N^2$ by 100.3°.

It is known [9, 18, 23] that in the acylation of NH_2OH a mixture of products of N- and O-monoacylation initially always formed. However the carbonyl group of the O-acyl derivatives in most cases reacts with excess NH_2OH, and the O-acylhydroxylamine converts into thermodynamically more stable hydroxamic acid. The latter is also valid for N,O-diacyl hydroxylamine derivatives that in reaction with excess NH_2OH give a double amount of hydroxamic acid [18]. However in our case the reaction products **III** and **IVa** do not react with excess NH_2OH at a notable rate (ratio **III** or **IVa**–NH_2OH 1 : 2, 20°C, 3 h). The XRD data for compound **IVa** make clear the reason of this unusual stability. The fragment O^1=C^5–C^3=C^2 of the O-acyl in **IVa** is virtually planar, and the electrophilicity of the carbonyl group is reduced by the conjugation with the C^2=C^3 bond. Besides, as seen from Fig. 1, the attack of the electrophilic atom C^5 with hydroxylamine is hampered by contiguous methyl groups C^{13} and C^{14}. Presumably the stability of O-acylhydroxylamine **III** against the action of excess NH_2OH is also underlain by the shielding of the carbonyl group and its conjugation with the C=C bond of the pyrroline ring. The stability of O-acyl derivatives of NH_2OH may also originate from the decrease in the electrophilicity of carbonyl groups under the effect of electron-donor substituents. For instance, in reaction of isatoic anhydride with NH_2OH a stable *O*-(2-aminobenzoyl)hydroxylamine [24] was obtained in 60% yield: Here the electrophilicity of the carbonyl carbon atom was reduced by the effect of the *ortho*-amino group, and also owing to the conjugation with the benzene ring.

Table 2. Bond lengths in molecule **IVa**

Bond	*d*, Å	Bond	*d*, Å
O^1–C^5	1.188(6)	O^2–C^5	1.372(5)
O^2–N^2	1.413(4)	O^3–C^6	1.195(6)
O^4–N^1	1.276(5)	O^5–N^3	1.258(5)
N^1–C^1	1.483(5)	N^1–C^4	1.481(5)
N^2–C^6	1.346(5)	N^3–C^8	1.472(5)
N^3–C^9	1.480(5)	C^1–C^2	1.486(6)
C^1–C^{11}	1.514(6)	C^1–C^{12}	1.531(7)
C^2–C^3	1.339(5)	C^3–C^5	1.478(6)
C^3–C^4	1.516(6)	C^4–C^{14}	1.516(7)
C^4–C^{13}	1.543(6)	C^6–C^7	1.488(6)
C^7–C^{10}	1.309(5)	C^7–C^8	1.495(6)
C^8–C^{15}	1.513(9)	C^8–C^{16}	1.533(8)
C^9–C^{10}	1.478(6)	C^9–C^{18}	1.524(8)
C^9–C^{17}	1.511(7)		

Triradical **V** may exist in the form of two isomers with different spatial arrangement of substituents at the C=N bond. In its turn, each of these isomers may have eight *s-cis-trans*-configurations of three conjugated double bonds. The molecular structure of triradical V we have isolated is presented in Fig. 2 and the bond distances and bond angles in this molecule are compiled in Tables 4, 5. Triradical **V** is a *Z*-isomer since its atoms O^2 and O^3 are located in a *cis*-position with respect to C^6=N^2 bond. The carbonyl groups in acyl fragments **B** and **C** are present in the *s-trans*-position relative to the double bonds of the pyrroline rings. The double bond C^6=N^2 is in a *s-trans*-position with respect to the double bond of the pyrroline ring **A**. Dihedral angles are $C^{10}C^7C^6N^2$ (2.4°), $C^2C^3C^5O^1$ (16.3°), and $C^{21}C^{20}C^{19}O^6$ (19.1°). The interatomic distances in the three flat pyrroline rings **A**–**C** are identical within 3σ and are close to those of fragment **B** in molecule **IVa**. This fact reflects the approximately equal extent of

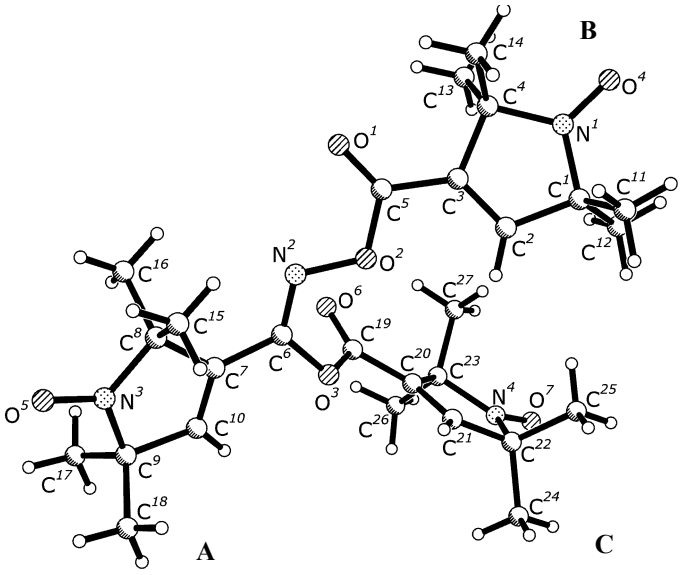


Fig. 2. Molecular structure of triradical **V**.

Table 3. Bond angles in molecule **IVa**

Angle	ω, deg	Angle	ω, deg
$C^5O^2N^2$	114.1(3)	$O^4N^1C^1$	122.1(3)
$O^4N^1C^4$	122.0(3)	$C^1N^1C^4$	115.7(3)
$C^6N^2O^2$	115.9(3)	$O^5N^3C^8$	122.3(4)
$O^5N^3C^9$	122.5(4)	$C^8N^3C^9$	115.2(3)
$N^1C^1C^2$	99.4(3)	$N^1C^1C^{11}$	110.1(3)
$C^2C^1C^{11}$	113.7(4)	$N^1C^1C^{12}$	109.3(4)
$C^2C^1C^{12}$	112.8(3)	$C^{11}C^1C^{12}$	110.9(4)
$C^3C^2C^1$	113.7(4)	$C^2C^3C^5$	121.9(4)
$C^2C^3C^4$	112.2(3)	$C^5C^3C^4$	125.8(3)
$N^1C^4C^3$	98.9(3)	$N^1C^4C^{14}$	110.0(4)
$C^3C^4C^{14}$	112.8(3)	$N^1C^4C^{13}$	108.7(3)
$C^3C^4C^{13}$	113.2(4)	$C^{14}C^4C^{13}$	112.4(4)
$O^1C^5O^2$	123.4(4)	$O^1C^5C^3$	126.6(4)
$O^2C^5C^3$	110.1(4)	$O^3C^6N^2$	123.2(4)
$O^3C^6C^7$	124.6(4)	$N^2C^6C^7$	112.2(4)
$C^{10}C^7C^8$	112.7(3)	$C^{10}C^7C^6$	127.2(4)
$C^8C^7C^6$	120.1(4)	$N^3C^8C^7$	99.1(3)
$N^3C^8C^{15}$	109.5(5)	$C^7C^8C^{15}$	111.2(4)
$N^3C^8C^{16}$	110.2(4)	$C^7C^8C^{16}$	113.1(5)
$C^{15}C^8C^{16}$	112.8(4)	$C^{10}C^9N^3$	98.9(3)
$C^{10}C^9C^{18}$	112.5(4)	$N^3C^9C^{18}$	109.9(5)
$C^{10}C^9C^{17}$	113.5(5)	$N^3C^9C^{17}$	111.0(4)
$C^{18}C^9C^{17}$	110.5(4)	$C^7C^{10}C^9$	114.2(4)

Table 4. Bond lengths in molecule **V**

Bond	*d*, Å	Bond	*d*, Å
O^2–C^5	1.369(4)	O^2–N^2	1.415(3)
O^3–C^6	1.379(4)	O^3–C^{19}	1.382(4)
O^6–C^{19}	1.194(4)	O^1–C^5	1.189(4)
O^7–N^4	1.271(3)	O^5–N^3	1.269(4)
N^2–C^6	1.274(4)	O^4–N^1	1.270(3)
N^3–C^8	1.480(4)	N^3–C^9	1.474(5)
N^4–C^{22}	1.462(5)	N^4–C^{23}	1.485(4)
C^8–C^7	1.511(5)	C^8–C^{16}	1.526(4)
C^8–C^{15}	1.529(5)	C^{20}–C^{21}	1.325(4)
C^{20}–C^{19}	1.461(4)	C^{20}–C^{23}	1.505(5)
N^1–C^4	1.486(4)	N^1–C^1	1.482(4)
C^6–C^7	1.454(4)	C^7–C^{10}	1.328(4)
C^2–C^3	1.314(4)	C^2–C^1	1.499(4)
C^{23}–C^{27}	1.523(5)	C^{23}–C^{26}	1.532(5)
C^{22}–C^{21}	1.488(5)	C^{22}–C^{24}	1.518(5)
C^{22}–C^{25}	1.529(4)	C^5–C^3	1.473(4)
C^3–C^4	1.515(4)	C^1–C^{12}	1.523(6)
C^1–C^{11}	1.515(5)	C^4–C^{14}	1.518(6)
C^4–C^{13}	1.525(5)	C^{10}–C^9	1.499(5)
C^9–C^{18}	1.513(6)	C^9–C^{17}	1.549(5)

conjugation of the double bonds C^6=N^2, C^5=O^1, and C^{19}=O^6 with the double bonds of rings **A**, **B**, and **C** respectively. The angles between the rings **A**, **B**, and **C** and virtually planar fragments $C^7C^6N^2O^3$, $C^3C^5O^1O^2$, and $C^{20}C^{19}O^3O^6$ amount respectively to 11.2, 15.8, and 16.8°.

The linear part of the molecule is characterized by dihedral angles $C^3C^5O^2N^2$ (11.1°), $O^1C^5O^2N^2$ (10.8°), $C^5O^2N^2C^6$ (10.8°), $O^2N^2C^6C^7$ (172.8°), $C^7C^6O^3C^{19}$ (57.2°), $C^6O^3C^{19}O^6$ (18.3°), and $O^3C^{19}C^{20}C^{21}$ (18.7°). The fragment $C^7C^6O^3N^2O^2$ is practically flat, the minimum deviation from the mean plane is 0.0035 Å for atom O^3, and maximum, 0.0429 Å for atom C^6. The length of the double bond C^6=N^2 equals 1.274(4) Å against 1.346(5) Å for analogous ordinary bond in molecule **IVa**. The bonds C^5=O^1 and C^{19}=O^6 are double bonds (Table 2), and all other bonds in chains C^7···C^3 and C^6···C^{20} are ordinary. According to our information, the structure of a tryacyl hydroxylamine derivative was established in this study for the first time.

The formation of triradical **V** at the acylation of compound **IVa** suggests that in the solution of compound

IVa a certain equilibrium concentration of tautomer **IVc** is present. Although its fraction in the equilibrium is insignificant and it has been impossible to detect it in the solution by IR spectroscopy, presumably the high nucleophilicity of its OH group ensures the high velocity and selectivity of the compound **IVa** acylation into triradical **V**. The hydroximic structure of **IVc** type failed to be detected by Schraml et al. [14] for the other N,O-diacyl derivatives, yet their ^{1}H NMR data indicated an exchange process in the NH group that might be caused by tautomerism.

EXPERIMENTAL

IR spectra were recorded in the range 400–4000 cm^{-1} on a spectrophotometer Specord 75IR from mulls in mineral oil or solutions in $CHCl_3$, UV spectra, on a spectrophotometer Specord UV-VIS from solutions in ethanol. ESR spectra were taken at room temperature on an EPA-2M instrument. Mass spectra were measured on a LTQFT instrument in the mode of negative ions registering by electrospray procedure, the voltage on the emitter needle 3 kV, charge rate 1 μl min^{-1}. The samples were dissolved in 50% aqueous MeCN. Determination accuracy ±0.01 mass unit. Electron impact mass spectra were registered on a Finnigan GC-MS instrument. The melting points were measured on a heating block RNMK. HPLC was performed on a chromatograph Milikhrom [column 2 × 64 mm, Separon C18 (5 μm), detection at 240 nm], eluent MeCN–0.1 M water solution of KH_2PO_4, 40 : 60 (**A**), 60:40 (**B**). Retention volumes of substances, μl, in eluent **A**: (**Ia**) 150, (**Ib**) 995, (**Ic**) 570, (**Id**) 430, (**Ie**) 980, (**IIa**) 200, (**III**) 270, (**IVa**) 530, (**IVb**) 390, (**V**) 3500, (**VI**) 1350, (**VII**) 440, (**VIII**) 2800; in eluent **B**: (**Ie**) 320, (**IIa**) 160, (**III**) 200, (**IVa**) 240, (**IVb**) 200, (**V**) 550, (**VI**) 370, (**VIII**) 500, (**IX**) 380. TLC was carried out on Silufol UV-254 plates.

Initial 2,2,5,5-tetramethyl-1-oxylopyrroline-3-carboxylic acid (**Ia**) and its ester **Ic** were prepared by procedure [25]. Acid chloride **Ib**, activated ester **Id**, and mixed anhydride **Ie** was obtained as described in [26–28] respectively. Hydroxylamine hydrochloride was recrystallized from methanol. The alcoholic solution of NH_2OH was prepared by procedure [29]. Triethylamine and acetonitrile were dried and distilled over KOH and P_2O_5 respectively.

X-ray diffraction study was carried out on an automatic four-circle diffractometer Bruker P-4 [graphite monochromator, λ(MoK_α) 0.71073 Å, 293 K, θ/2θ-scanning]. In the experiment plate single crystals were used of compounds **IVa** and **V** of the size 0.15 × 0.1 × 0.05 mm. The parameters of unit cell were determined and refined by 35 reflections measured in the angle range

Table 5. Bond angles in molecule **V**

Angle	ω, deg	Angle	ω, deg
$C^5O^2N^2$	112.6(2)	$C^6O^3C^{19}$	117.7(2)
$C^6N^2O^2$	109.8(2)	$O^5N^3C^8$	122.3(3)
$O^5N^3C^9$	121.9(3)	$C^8N^3C^9$	115.8(3)
$O^7N^4C^{22}$	123.0(3)	$O^7N^4C^{23}$	121.8(3)
$C^{22}N^4C^{23}$	114.9(2)	$N^3C^8C^7$	99.0(2)
$N^3C^8C^{16}$	110.3(3)	$C^7C^8C^{16}$	112.9(3)
$N^3C^8C^{15}$	109.1(3)	$C^7C^8C^{15}$	114.0(3)
$C^{16}C^8C^{15}$	110.8(3)	$C^{21}C^{20}C^{19}$	125.3(3)
$C^{21}C^{20}C^{23}$	112.4(3)	$C^{19}C^{20}C^{23}$	122.1(3)
$O^4N^1C^4$	122.3(3)	$O^4N^1C^1$	122.7(3)
$C^4N^1C^1$	115.0(2)	$N^2C^6O^3$	123.8(2)
$N^2C^6C^7$	120.7(3)	$O^3C^6C^7$	115.2(3)
$C^{10}C^7C^6$	124.2(3)	$C^{10}C^7C^8$	112.2(3)
$C^6C^7C^8$	123.6(3)	$C^3C^2C^1$	113.3(3)
$N^4C^{23}C^{27}$	109.9(3)	$N^4C^{23}C^{20}$	99.2(3)
$C^{27}C^{23}C^{20}$	113.6(3)	$N^4C^{23}C^{26}$	108.2(3)
$C^{27}C^{23}C^{26}$	112.0(3)	$C^{20}C^{23}C^{26}$	113.1(3)
$N^4C^{22}C^{21}$	100.1(2)	$N^4C^{22}C^{24}$	111.4(3)
$C^{21}C^{22}C^{24}$	113.2(3)	$N^4C^{22}C^{25}$	109.6(3)
$C^{21}C^{22}C^{25}$	112.3(3)	$C^{24}C^{22}C^{25}$	109.9(3)
$O^1C^5O^2$	123.6(3)	$O^1C^5C^3$	126.4(3)
$O^2C^5C^3$	110.0(3)	$C^{20}C^{21}C^{22}$	113.1(3)
$C^2C^3C^5$	126.2(3)	$C^2C^3C^4$	113.1(3)
$C^5C^3C^4$	120.6(3)	$N^1C^1C^2$	99.4(3)
$N^1C^1C^{12}$	109.5(3)	$C^2C^1C^{12}$	114.4(3)
$N^1C^1C^{11}$	110.9(3)	$C^2C^1C^{11}$	111.7(3)
$C^{12}C^1C^{11}$	110.4(3)	$N^1C^4C^{14}$	109.4(3)
$N^1C^4C^{13}$	109.8(3)	$C^{14}C^4C^{13}$	112.3(3)
$N^1C^4C^3$	98.8(2)	$C^{14}C^4C^3$	113.6(3)
$C^{13}C^4C^3$	112.0(3)	$O^6C^{19}O^3$	122.1(3)
$O^6C^{19}C^{20}$	127.1(3)	$O^3C^{19}C^{20}$	110.8(3)
$C^7C^{10}C^9$	113.7(3)	$N^3C^9C^{10}$	99.0(2)
$N^3C^9C^{18}$	111.0(3)	$C^{10}C^9C^{18}$	113.2(3)
$N^3C^9C^{17}$	108.8(3)	$C^{10}C^9C^{17}$	113.4(3)
$C^{18}C^9C^{17}$	110.9(4)		

θ 10–15°. The experimental reflections array was obtained in the angle range θ 2.46–24.99°. The structures were solved by the direct method. The positions and thermal parameters of the nonhydrogen atoms were refined in isotropic and further in anisotropic approximation by the full-matrix least-squares method. Atomic coordinates and equivalent thermal parameters are available from the authors. Hydrogen atoms were revealed from the difference Fourier synthesis and were not taken into the refinement. All calculations were carried out with the use of SHELXTL software [30].

For biradical **IVa** overall number of independent reflections 1802, 1425 with intensity $I > 2\sigma(I)$. The main crystallographic parameters: *a* 8.151(2), *b* 11.287(2), *c* 11.014(2) Å, $\alpha = \gamma = 90°$, β 91.86(3)°, *V* 1012.8(4) Å^3, d_{calc} 1.198 g/cm^3, space group $P2_1$, *Z* 2. Final divergence factors: R_1 0.0439 for reflections with $I > 2\sigma(I)$, R_2 0.0584 for all reflections. *GOOF* 1.027.

For triradical **V** overall number of independent reflections 2925, 2526 with intensity $I > 2\sigma(I)$. The main crystallographic parameters: *a* 11.544(2), *b* 13.448(3), *c* 19.896(4) Å, $\alpha = \beta = \gamma = 90°$, *V* 3088.7(11) Å^3, d_{calc} 1.143 g/cm^3, space group $P2_12_12_1$, *Z* 4. Final divergence factors: R_1 0.0376 for reflections with $I > 2\sigma(I)$, R_2 0.0465 for all reflections. *GOOF* 0.996.

Reaction of 3-carboxy-2,2,5,5-tetramethylpyrrolin-1-oxyl (Ia) with hydroxylamine. Carbodiimide procedure. To a mixture of 203 mg (1 mmol) of acid **Ia** and 85 mg (1.2 mmol) of $NH_2OH·HCl$ in 4 ml of MeCN at cooling with ice was added while stirring in succession 251 mg of dicyclohexylcarbodiimide and 0.17 ml of Et_3N. After 10 min the cooling was removed, and the stirring was continued for 4 h more at ~20°C. Further to the reaction mixture 4 ml of ether was added, the mixture was left standing for 30 min, the precipitate was filtered off and washed on the filter by a mixture MeCN–ether, 1 : 1. Yields of the reaction products present in the mixture are reported in Table 1. The yellow solution obtained was subjected to chromatography on a column 30 × 60 mm packed with silica gel preliminary washed with with dilute HCl to remove iron-containing impurities. The elution was carried out first with ether, than with ethyl acetate to obtain a fraction with pure acid **IIa**. On distilling off the solvent we obtained in the residue 85 mg (39%) of compound **IIa**, yellow prismatic crystals, mp 180–181.5°C (decomp.) [1].

Reaction of acid chloride Ib with NH_2OH in the presence of Et_3N. The reaction between 1.22 g (6 mmol) of acid chloride **Ib**, 0.63 g (9 mmol) of $NH_2OH·HCl$, and 1.67 ml (12 mmol) of Et_3N in 12 ml of MeCN was performed as described in [1]. The composition of reaction products determined by HPLC is reported in Table 1. Acid **IIa** was isolated from the reaction mixture in 54% yield

Reaction of acid chloride Ib with NH_2OH in the presence of pyridine. To a solution of 405 mg (2 mmol) of acid chloride **Ib** in 4 ml of MeCN at ~20°C was added while stirring in succession 78 mg (1.1 mmol) of $NH_2OH·HCl$ and 237 mg (3 mmol) of pyridine. After 20 min the reaction mixture was diluted with 10 ml of anhydrous ether. The solution was separated from the formed precipitate and was evaporated in a vacuum. The residual oily substance was extracted with ether (10 ml), and the extract was evaporated to give 360 mg of products mixture whose yields are compiled in Table 1. The chromatographic separation of the mixture on silica gel provided a fraction (150 mg) containing mainly biradical **IVa** and triradical **V**. By crystallization of this mixture from benzene and toluene we obtained 50 mg of biradical **IVa**, fine yellow prismatic crystals, mp156–158°C. For the isolation of triradical **V** the benzene mother liquor of the previous crystallization was evaporated to dryness. The residue was recrystallized in succession from cyclohexane and MeCN to obtain 15 mg of pure compound **V**, yellow needle crystals, mp 187–189°C.

Reaction of methyl ester Ic with NH_2OH. To 210 mg (1 mmol) of compound **Ic** under an argon atmosphere at ~20°C was added 1 ml of freshly prepared 2 M solution of NH_2OH in EtOH. For monitoring with HPLC the samples of reaction mixture were diluted with MeOH to a concentration of ~2 mg/ml, and chromatograms were registered under above mentioned conditions. In 20 h ~65% of initial compound **Ic** was consumed, and the ratio of yields of compounds **IIa**, **III**, and **VII** was 3 : 1 : 60. Reaction product **VII** was identified by comparison of UV spectra and retention volume with an authentic sample prepared by the reduction of compound **Ic** with methanol solution of HCl [31] (20 mg of **Ic**, 0.1 ml of 2N HCl, MeOH, ~20°C, 1 h).

Reaction of activated ester Id with NH_2OH. To a suspension of 281 mg (1 mmol) of ester **Id** in 2 ml of MeOH at ~20°C was added dropwise within 5 min while stirring 1.3 ml of freshly prepared 1 M solution of NH_2OH in MeOH. The reaction was monitored by TLC and HPLC. In 15 min after the start of the reaction we found by TLC (eluent $CHCl_3$–MeCN, 5 : 2) in the reaction mixture compounds **IIa** (R_f 0.08), **III** (R_f 0.75), and

N-hydroxysuccinimide (R_f 0.15). Yields of the products are given in Table 1. After 30 min the reaction mixture was evaporated to obtain yellow oily substance. By flash-chromatography on silica gel (eluent $CHCl_3$–MeCN, 10 : 1) we isolated from this residue 142 mg (71%) of **3-(aminooxycarbonyl)-2,2,5,5-tetramethylpyrrolin-1-oxyl (III),** yellow crystals, mp 95–98°C (decomp.). UV spectrum (EtOH), λ_{max}, nm (e, l mol^{-1} cm^{-1}): 214 (1.13 ч 10^4). IR spectrum, ν, cm^{-1} (mineral oil): 3077 (H–C=C), 1722 (C=O), 1631 (C=C), 3270, 3195 1572 (NH_2); ($CHCl_3$): 1729 (C=O), 1629 (C=C), 3319, 3229, 1553 (NH_2). ESR spectrum (H_2O): 3 lines, a_N 1.63 μT. Mass spectrum, *m*/*z* (I_{rel}, %): 198.09 (3) [*M* – H]$^-$ (calculated [*M* – H]$^-$ 198.1004), 197.09 (5) [*M* – H_2]$^-$, 183.27 (100) [*M* – CH_4]$^-$, 168,18 (6) [*M* – HNO]$^-$, 124.18 (2), 113.09 (6). Found, %: C 54.05; H 7.48; N 13.97. $C_9H_{15}N_2O_3$. Calculated, %: C 54.26; H 7.59; N 14.06., *M* 199.23.

Reaction of mixed anhydride Ie with **NH_2OH.** To a solution of 26 mg (0.1 mmol) of compound **Ie** in 0.3 ml of solvent indicated in Table 1 was added 0.08 ml of freshly prepared 2 M solution of NH_2OH in anhydrous EtOH. In 15 min after the start of the reaction we found by TLC (eluent $CHCl_3$–MeCN, 5 : 1) in the reaction mixture compounds **Ia** (R_f 0.29), **IIa** (R_f 0.04), **III** (R_f 0.47), **IVa** (R_f 0.57). Yields of products according to HPLC data are given in Table 1.

***N,O*-Bis[(2,2,5,5-tetramethyl-1-oxylopyrrolin-3-yl)carbonyl]hydroxylamine (IVa).** (a) To a solution of 203 mg (1.02 mmol) of compound **IIa** and 117 mg (1.16 mmol) of Et_3N in 1 ml of MeCN at cooling with ice was added at stirring within 10 min a solution of 203 mg (1 mmol) of acid chloride **Ib** in 0.5 ml of MeCN. The mixture was stirred for 10 min at cooling and then 1.5 h at ~20°C. According to HPLC the yields of reaction products in the mixture were as follows (%): **Ia** 2, **IIa** 2, **IVa** 88, **IVb** 4, **V** 5, **VI** 1. The separated precipitate of Et_3N·HCl with admixture of triradical **V** was filtered off, the yellow solution obtained was evaporated in a vacuum, the residue was treated with 1 ml of water. The formed crystals were filtered off, washed with water, and dried. Yield of compound **IVa** 242 mg (66%), yellow prismatic crystals, mp 156–158° (toluene). UV spectrum (EtOH), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 213 (2.21×10^4). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3200 (NH), 1769 (OC=O), 1705 (NC=O), 1629 (C=C). ESR spectrum (benzene, ~20°C): triplet of triplets with amplitudes ratio (38 : 100 : 75) : (37 : 88 : 30) : (71 : 92 : 27), a_N 1.42 μT. Mass spectrum, *m*/*z* (I_{rel}, %): 364.18 (60) [*M* – H]$^-$ (calculated [*M* – H]$^-$ 364.1872), 223.18 (4), 198.18 (5) [$C_9H_{14}N_2O_3$]$^-$, 183.18 (100) [$C_8H_{11}N_2O_3$]$^-$, 168.18 (7) [$C_9H_{14}NO_2$]$^-$, 124.09 (2). Found, %: C 59.37; H 7.51; N 11.40. $C_{18}H_{27}N_3O_5$. Calculated, %: 59.16; H 7.45; N 11.50. *M* 365.43.

After isolation of compound **IVa** in the water mother liquor accumulated the isomeric biradical with spectral characteristics consitent with the structure of compound **IVb**. UV spectrum of this biradical in eluent A contains a single band, λ_{max} 218 nm, and ESR spectrum, three lines with a_N 1.60 μT. ESR spectrum of the benzene solution of the presumed compound **IVb** contained five lines with the amplitudes ratio 100 : 19 : 121 : 17 : 90, a_N 1.47 μT.

b. A mixture of 100 mg (0.50 mmol) of compound **III** and 131 mg (0.51 mmol) of anhydride **Ie** was dissolved in 0.7 ml of MeCN and left standing for 4 days at ~20°C. As shown by HPLC, the reaction product contained 75% of biradical **IVa**, 4% of anhydride **VI**, and 5% of presumed triradical **VIII**. The obtained yellow solution was worked up similarly to the preceding experiment to get 106 mg (58%) of compound **IVa**, mp 156–158° (toluene).

3-{[(2,2,5,5-Tetramethyl-1-oxylopyrrolin-3-yl)carbonyloxyimino][(2,2,5,5-tetramethyl-1-oxylopyrrolin-3-yl)carbonyloxy]methyl}-2,2,5,5-tetramethylpyrrolin-1-oxyl (V). (a) A solution of 100 mg (0.5 mmol) of hydroxamic acid **IIa** and 56 mg (0.55 mmol) of Et_3N in 0.4 ml of MeCN was added while stirring and cooling with cold water to a solution of 203 mg (1 mmol) of acid chloride **Ib** in 0.4 ml of MeCN. The stirring at ~20°C was continued for 1 h. Then at stirring the mixture was treated with 0.8 ml of water and left standing till the end of crystallization. The precipitated reaction product was filtered off, washed with 50% aqueous MeCN, and dried. Yield 242 mg (91%), yellow prismatic crystals, mp 187–189°C (aqueous MeCN). UV spectrum (EtOH), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 222 (3.04×10^4), 244 (2.43×10^4). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1760 (C=O), 1631 (C=C), 1602 (C=N). ESR spectrum (benzene, ~25°C): 7 lines with the amplitudes ratio 49 : 63 : 68 : 100 : 58 : 55 : 45, a_N 1.48 μT. Mass spectrum, *m*/*z* (I_{rel}, %): 530.26 (1) [*M* – H]$^-$ (calculated [*M* – H]$^-$ 530.2740), 183.18 (100) [$C_8H_{11}N_2O_3$]$^-$, 168.14 (3) [$C_9H_{14}NO_2$]$^-$, 143.09 (3), 113.09 (4). Found, %: C 61.25; H 7.43; N 10.30. $C_{27}H_{39}N_4O_7$. Calculated, %: C 61.00; H 7.39; N 10.54. *M* 531.63.

b. A solution of 61 mg (0.3 mmol) of acid chloride **Ib** in 0.8 ml of MeCN was added within 10 min at stirring to a mixture cooled with ice of 100 mg (0.27 mmol) of biradical **IVa** and 36 mg (0.36 mmol) of Et_3N in 0.8 ml

MeCN. The mixture was stirred for 15 min at cooling, then 4 h at ~20°C. Then the solvent was distilled off at a reduced pressure, and the residue was treated with 1 ml of water. The precipitated reaction product was filtered off, washed with water, and dried. Yield 121 mg (83%), mp 187–189°C (aqueous MeCN).

2,2,5,5-Tetramethyl-1-oxylopyrrolin-3-carboxanhydride (VI). To a solution of 100 mg (0.5 mmol) of ester **III** and 61 mg (0.6 mmol) of Et_3N in 0.4 ml of anhydrous MeCN at cooling with ice while stirring was added within 10 min a solution of 104 mg (0.51 mmol) of acid chloride **Ib** in 0.4 ml MeCN. The mixture was stirred for 10 min at cooling, then 45 min at ~20°C. By HPLC data the yields of reaction products in the mixture were as follows, %: **Ia** 2, **IVa** 1, **V** 4, **VI** 92, **VIII** 1. The separated precipitate composed of $Et_3N{\cdot}HCl$ and triradical **V** was filtered off. The obtained yellow solution was concentrated in a vacuum and worked up as described above.. Yield 143 mg (81%), yellow plate crystals, mp 142–144°C (cyclohexane) (141.5–143°C [26]). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1783 and 1727 (C=O), 1624 (C=C), 1125 and 997 (O=C–O–C=O). ESR spectrum (benzene, ~25°C): 9 lines with amplitudes ratio 2:100:22:15:105:9:24:99:2, a_N 1.43 μT.

3-(3-Nitrobenzylideneaminooxycarbonyl)-2,2,5,5-tetramethylpyrrolin-1-oxyl (IX). To a solution of 100 mg (0.5 mmol) of ester **III** and 114 mg (0.75 mmol) of *m*-nitrobenzaldehyde in 0.5 ml of methanol was added 90 mg (1.5 mmol) of acetic acid. The reaction mixture was brought to boiling and then left standing for 5 h at ~20°C. The separated precipitate was filtered off, washed with MeOH, and dried in a vacuum. Yield 155 mg (93%), yellow needle crystals, mp 156–157° (MeOH). UV spectrum (EtOH), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 301 sh (1.48×10^3), 251 (2.49×10^4), 225 sh (1.63×10^4). IR spectrum (mineral oil), ν, cm^{-1}: 3097, 3080, 3068, 3060 (Ph and H–C=C), 1745 (C=O), 1630, 1619, 1611 (Ph and C=C), 1572 (C=N), 1532, 1354 (NO_2). ESR spectrum (benzene, ~25°C): 3 lines, a_N 1.48 μT. Mass spectrum (electron impact, 70 eV), *m*/*z* (I_{rel}, %): 332 (46) $[M]^+$, 318 (3), 302 (1) $[M - NO]^+$, 184 (11) $[RCO_2H]^+$, 167 (96) $[RCO]^+$, 154 (42), 153 (69), 152 (71), 150 (33), 148 (17), 139 (38), 137 (39), 125 (20), 109 (100). Found, %: C 57.91; H 5.31; N 12.73. $C_{16}H_{18}N_3O_5$. Calculated, %: C 57.83; H 5.46; N 12.64. *M* 332.

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