# 1,3-Dipolar cycloaddition in the synthesis of pyrazolyl-substituted nitronyl nitroxides*

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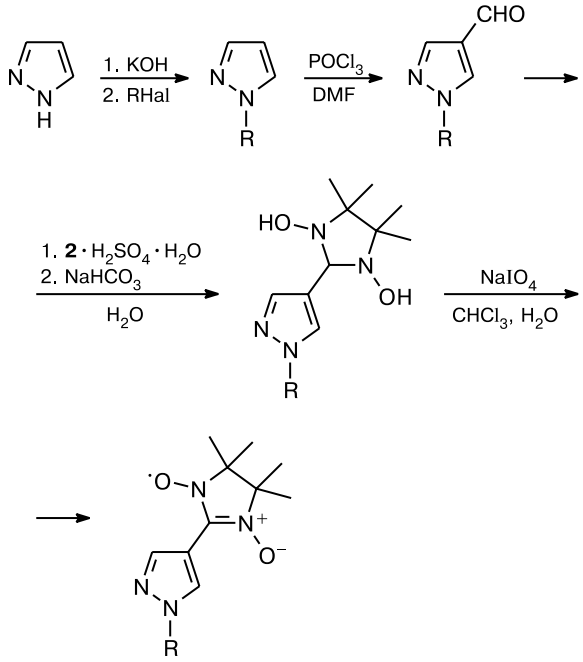
A new approach to the synthesis of polyfunctional pyrazolyl-substituted nitronyl nitroxides was developed based on the presynthesized pyrazole derivatives prepared by 1,3-dipolar cycloaddition. The structures of the resulting mono- and biradicals were confirmed by X-ray diffraction.

**Key words:** nitronyl nitroxide radicals, 1,3-dipolar cycloaddition, pyrazole, X-ray diffraction analysis.

The complexes of $Cu(hfac)_2$ with 2-(1-alkyl-1*H*-pyrazol-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (**1**) have a unique ability to undergo specific magnetic-structural phase transitions, which are manifested in the temperature dependence of the effective magnetic moment ($\mu_{eff}$) as anomalies similar in character to spin transitions. This ability has attracted great interest[1,2] and stimulated the development of the chemistry of spin-labeled pyrazoles.[3] The synthesis of "symmetrical" (with respect to donor groups) nitroxides, which can serve as parent compounds of pyrazole-substituted mono- and bis-nitronyl nitroxides, has attracted our attention. A known approach[4,5] to the synthesis of mononitroxides **1** involves *N*-alkylation of pyrazole followed by formylation of the resulting *N*-alkylpyrazole, condensation of *N*-alkylpyrazole-4-carbaldehyde with 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate ($\mathbf{2}\cdot H_2SO_4\cdot H_2O$), and oxidation of 1,3-dihydroxyimidazolidine to form nitronyl nitroxide (Scheme 1).

A weak point of the synthetic sequence is that formylation is characterized by an unstable yield (20—60%). In addition, the severe conditions of this step ($POCl_3$, 130—150 °C) substantially limit the possibility of the synthesis of pyrazolyl-substituted nitronyl nitroxides and imino nitroxides. This stimulated us to develop an efficient procedure for the synthesis of *N*-unsubstituted spin-labeled pyrazole **1a** (R = H), because the presence of a reliable and easily scalable method for the preparation of this compound opens wide possibilities for the synthesis of paramagnetic pyrazole derivatives, including *N*-functionalization of the pyrazole ring. When solving this problem, we rejected the classical method[6] based on the use of pyrazole-4-carbaldehyde, which is difficult to synthesize,[7] and examined the possibility of using 1,3-dipolar cycloaddition of diazomethane to propiolaldehyde acetal as the initial step. In the present study, we demonstrated that

**Scheme 1**




**1**

R = Me, Et, Pr, Pr$^i$, Bu

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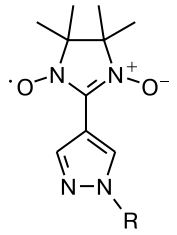
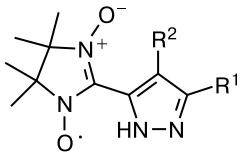
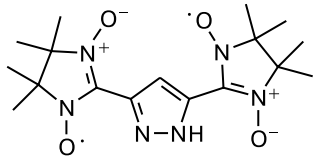
this approach allows one to prepare the previously inaccessible polyfunctional mononitroxides **3a—c** and bis(nitronyl nitroxide) **4**.



**1a,b**



**3a—c**



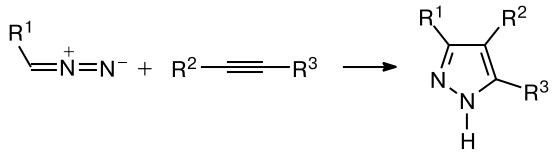
**4**

**1:** R = H (**a**), Me (**b**)
**3:** $R^1 = R^2$ = H (**a**), $R^1 = R^2$ = COOEt (**b**), $R^1$ = COOEt, $R^2$ = H (**c**)

## Results and Discussion

The synthetic scheme used in the present study involves 1,3-dipolar cycloaddition of the diazo compound $R^1—CH=N_2$ to the corresponding alkyne $R^2—C\equiv C—R^3$ (Scheme 2). The resulting pyrazole derivatives can be transformed into the target nitroxides.

**Scheme 2**

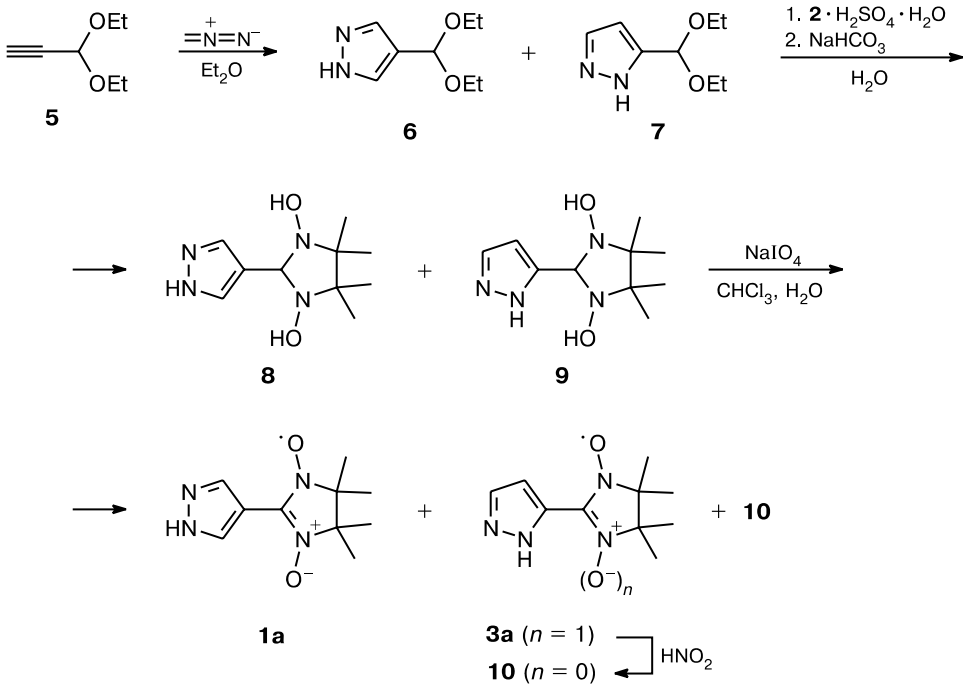


Cycloaddition is known to afford predominantly 3(5)-substituted pyrazoles[8] if a substituent in alkyne exerts the $-M$ effect. This fact is confirmed by the reaction of $CH_2=N_2$ with HC≡C—CHO giving rise to pyrazole-3(5)-carbaldehyde.[9] Hence, the synthesis of pyrazole-4-carbaldehyde, which is a precursor of **1a** (R = H), required that the reaction of $CH_2=N_2$ be performed with alkyne containing such a synthetic equivalent of carbaldehyde that, upon cycloaddition, will find itself at position 4 of the pyrazole ring. It should be noted that the pathway of this reaction with alkynes bearing $-I,+M$ or $-I$ substituents is difficult to predict.[10,11] Nevertheless, the absence of the ability of the substituent to exert a mesomeric effect and an increase in the volume of the substituent would be expected to be favorable for the formation of 4-substituted pyrazoles. Hence, we decided to perform the reaction of diazomethane with 3,3-diethoxypropyne (**5**) (Scheme 3). At room temperature, the reaction in $Et_2O$ in the presence of a rather large excess of $CH_2=N_2$ is completed within several days. It is important that subsequent methylation of pyrazole with diazomethane under these conditions occurs much more slowly (according to the TLC data, the final product contained an insignificant amount of **1b**, where R = Me). The reaction afforded a viscous oily product, which was a complex mixture ($^1$H NMR data) containing predominantly acetals **6** and **7**. Attempts to separate a mixture of acetals or isolate pyrazole-4-carbaldehyde from the hydrolysis product of the mixture failed. Because of this, the viscous oily product was subjected to condensation with $\mathbf{2}\cdot H_2SO_4\cdot H_2O$ with the aim of obtaining a mixture of isomeric 1,3-dihydroxyimidazolidines **8** and **9**, which were oxidized with $NaIO_4$ without isolation. The resulting mixture can be separated by chromatography, and nitroxides **1a** and **3a** can be rather easily isolated from this mixture (see Scheme 3). This procedure for the synthesis is reliable, easily scalable, and allows the preparation of nitroxides **1a** and **3a** in 25 and 6% yields, respectively, based on the starting **5** (see Scheme 3). This reaction also affords other products in small amounts. One of these products is imino nitroxide **10**, whose formation was confirmed by a comparison with an authentic sample prepared by reduction of **3a**.

It should also be noted that we succeeded in growing high-quality single crystals of nitroxides **1a**, **3a**, and **10** and established their molecular and crystal structures. Since compound **1a** is readily available, it was used as the starting reagent for the preparation of new nitroxides **1** (Scheme 4) and, primarily, for the synthesis of sufficient amounts of isotopically substituted compounds **1c,d** (R = $CD_3$ and $C_2D_5$, respectively). The molecular structures of **1c,d** are shown in Fig. 1. The structural parameters are given in the Experimental section. These nitroxides were used in the synthesis of heterospin complexes, which can show specific thermally induced spin transitions, and in the detailed analysis of magnetic anomalies inherent in the nature of these complexes.[1] The above example shows that the possibility of alkylation of **1a** combined with the above-described procedure for its preparation extends the scope of the synthesis of the desired nitroxides necessary for the subsequent design of high-dimensional heterospin systems.

We used alkynes **11a—c** and 2,2-dimethoxy-1-diazoethane as substrates for the formation of formylpyrazoles, which are required for the preparation of nitroxides **3** and **4**. This approach allows one to rather easily prepare aldehyde acetal **12a**, from which nitroxide biradical **4** was synthesized (see below). Based on this method, we developed approaches to the synthesis of formylpyrazolecarboxylates **13** with the desired arrangement of functional groups (Scheme 5).

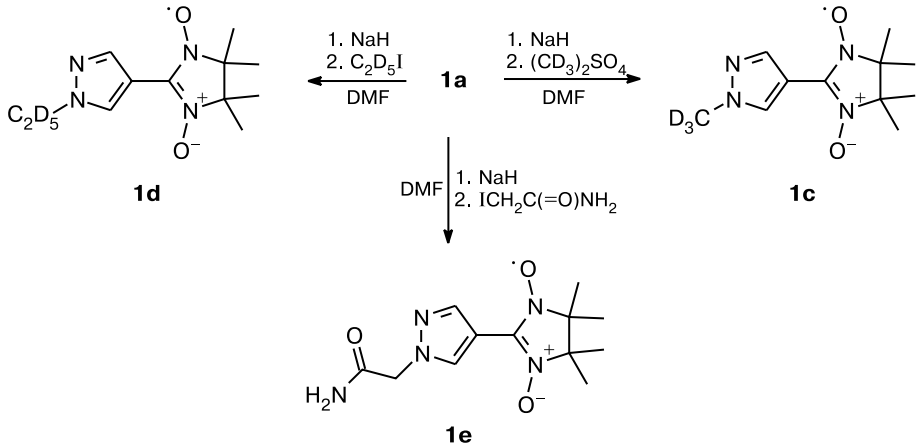
**Scheme 3**




Condensation of aldehydes **13a,b** with 2,3-bishydroxyamino-2,3-dimethylbutane (**2**) in MeOH affords 1,3-dihydroxyimidazolidines **14a,b**, which are oxidized with $NaIO_4$ in a two-phase $CHCl_3$—water system to give radicals **3b,c** (see Scheme 5). Nitronyl nitroxide **3b** is an oil. However, we succeeded in growing single crystals of hydroxyamine precursor **14a** and determined its structure (Fig. 2). In molecule **14a**, the imidazolidine ring adopts an envelope conformation. The hydroxy groups are located on one side of the plane of the ring. The N—O distances (1.437(3) and 1.453(3) Å) are slightly longer than those typical of sterically hindered hydroxylamines (1.396 Å)[12] due to formation of numerous hydrogen bonds between the hydroxy groups, the —NH— fragments, the carbonyl O atoms of the ester groups, and the N atoms of the pyrazole ring in the solid state.

The synthesis of nitroxide **3c** requires unusual conditions because the reaction with the use of the calculated **14b** : $NaIO_4$ ratio of 1 : 1.5 affords a green product (presumably, a mixture of products). We did not perform a special study of the nature of this product. Let us only note that an increase in the rate of addition of $NaIO_4$ to a

**Scheme 4**



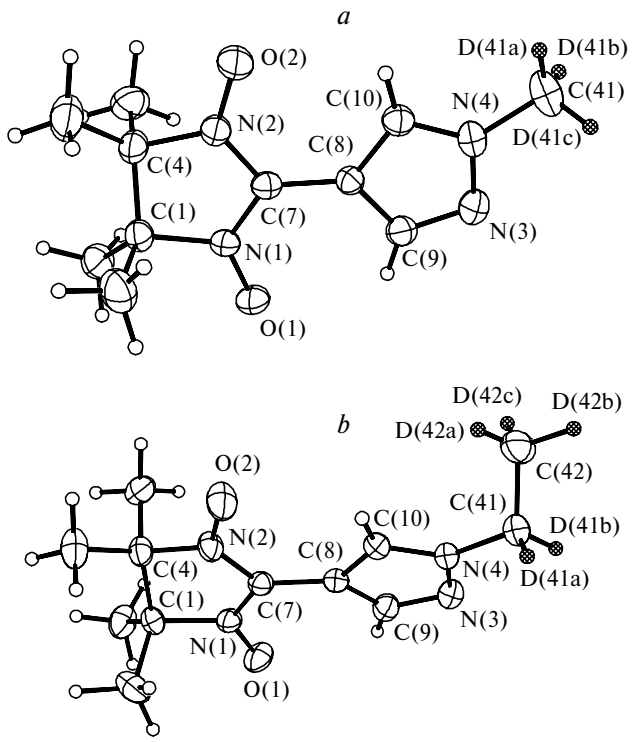



**Fig. 1.** Molecular structures of isotopically substituted compounds **1c** ($R = CD_3$) (*a*) and **1d** ($R = C_2D_5$) (*b*).

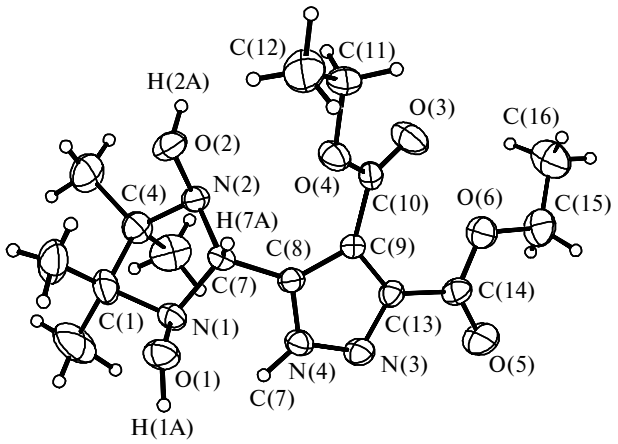
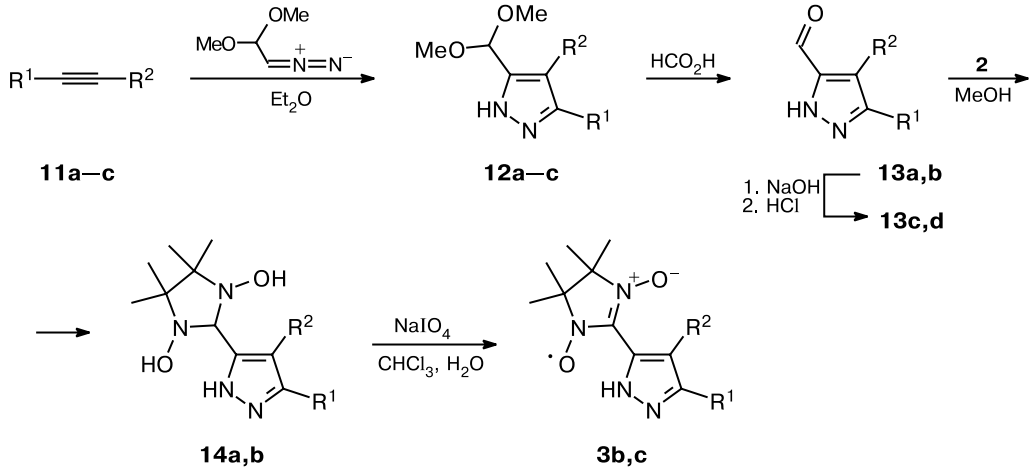



**Fig. 2.** Molecular structure of compound **14a**.

suspension of **14b** in a $CHCl_3$—$H_2O$ mixture led to intensification of the yellow tint in the color of this product. We varied the experimental conditions of the synthesis and found that the molar ratio **14b** : $NaIO_4$ = 1 : 0.6 is optimum for the synthesis of the target compound **3c**. A white precipitate is rapidly formed in the aqueous phase regardless of the rate of addition of the oxidizer to the $CHCl_3$—**14b**—$H_2O$ system, and the organic layer turns pale greenish-blue. Further mixing of the reaction mixture for 1 h leads to the disappearance of this precipitate, and the organic layer turns bright blue. Dark-blue crystals of **3c** can be isolated from the extract in chloroform in 90—94% yield. These data suggest that nitronyl nitroxide **3c** is sensitive to the presence of a large amount of $NaIO_4$ or its reduction products in the reaction mixture. It could be assumed that, after the addition of $NaIO_4$, oxidation occurs in an autocatalytic mode. However, virtually no formation of compound **3c** occurs in the presence of a smaller amount of $NaIO_4$ in the reaction mixture.

The solid phase of **3c** consists of dimeric molecules formed through H bonds (see Fig. 3). The N—O distances in molecule **3c** (1.277(5) and 1.280(5) Å) are typical of nitroxides.

**Scheme 5**




| | 11a, 12a | 3b, 11b, 12b | 3c, 11c, 12c | 13a, 14a | 13b, 14b | 13c | 13d |
|---|---|---|---|---|---|---|---|
| $R^1$ | CHO | COOEt | COOEt | COOEt | COOEt | COOH | COOH |
| $R^2$ | H | COOEt | H | COOEt | H | COOH | H |

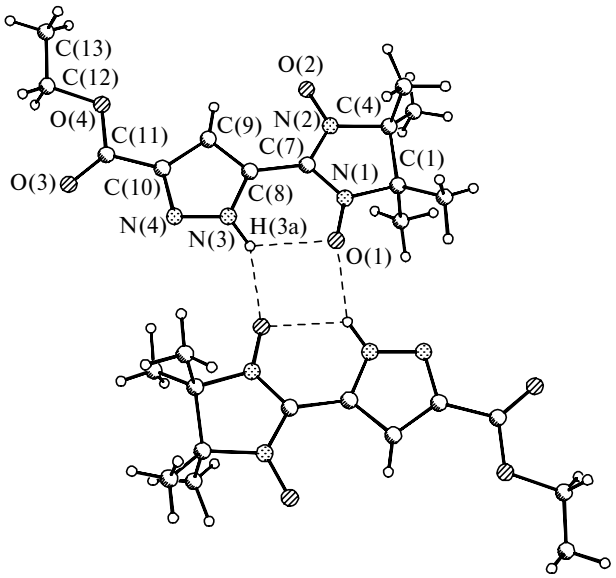



**Fig. 3.** Mode of dimerization of molecules **3c** (the hydrogen atoms of the alkyl groups are omitted).

In the course of oxidation of **14a** giving rise to nitronyl nitroxide, we attempted to replace $NaIO_4$ with $PbO_2$, which is widely used for this purpose.[13] As a result, we prepared a product, whose crystallization from an $H_2O$—MeOH mixture afforded an X-ray amorphous black-blue film that cracked during drying. Recrystallization of this product from $CH_2Cl_2$—heptane, $CH_2Cl_2$—ethyl acetate, or acetone—toluene mixtures afforded a finely dispersed blue powder, which did not allow us to study its structure by X-ray diffraction. Elemental analysis of this product showed that its composition corresponds to the formula $Pb_3O_2$(**3b**´)$_2$, where **3b**´ is deprotonated compound **3b**. The high-temperature asymptotics of the magnetic moment $\mu_{eff}$, which was calculated with the use of the molecular weight of $Pb_3O_2$(**3b**´)$_2$ (Fig. 4), also agrees well with the theoretical magnetic moment for biradicals (2.45 $\mu_B$).

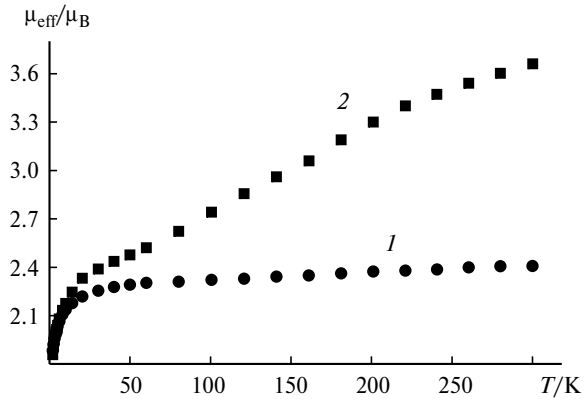



**Fig. 4.** Temperature dependences of the effective magnetic moments for $Pb_3O_2$(**3b**´)$_2$ (*1*) and Ni(**3b**´)$_2 \cdot 2H_2O$ (*2*).

Undoubtedly, the formation of the lead complex is evidence that the molecular structure of **3b** is favorable for the chelate formation. Hence, we decided to oxidize **14a** with $Ni_2O_3$ with the aim of preparing the $Ni^{II}$ complex with **3b**´ as the final product. The data from elemental analysis, IR spectroscopy, and magnetochemistry (see Fig. 4) for this product completely confirm our assumption. These data show that the smallest formula unit corresponding to this product is Ni(**3b**´)$_2 \cdot 2H_2O$. We believe that the above-described method for the synthesis of coordination compounds, which are formed by oxidation of 1,3-dihydroxyimidazolidines with high oxidation state transition metal oxides, can be used to prepare heterospin systems.

The formation of lead complexes appeared to be useful in the synthesis of pyrazolecarboxylic acids **3d,e**. Since aldehydes **13c,d** are very poorly soluble in $H_2O$, MeOH, EtOH, and THF, they virtually do not react with **2**.

Solutions of potassium salts of acids **13c,d** rapidly reacted with hydrosulfate **2** in a MeOH—$H_2O$ mixture to form the corresponding 1,3-dihydroxyimidazolidine derivatives, which were oxidized with $PbO_2$ without isolation. The reaction with **13c** afforded a paramagnetic salt. The elemental analysis data for this compound are most consistent with the composition $K_3$**3d**´. In the case of acid **13d**, the lead complex Pb(K**3e**´)$_2$ was isolated, where **3d**´ and **3e**´ are deprotonated pyrazole derivatives of the corresponding di- and monocarboxylates. Crystallization from a MeOH—toluene mixture gave Pb(K**3e**´)$_2$ as the solvate with MeOH (Scheme 6).

Treatment of an ethanolic solution of $K_3$**3d**´ with two equivalents of $H_2SO_4$ in EtOH resulted in a change in the color of the reaction mixture from violet to red. An attempt to crystallize the reaction products led to the formation of a finely dispersed yellow powder and pale brown crystals. The crystals were suitable for X-ray diffraction, which allowed us to study the structure of this product. The crystals are composed of the ions of compounds **15** (Fig. 5) generated as a result of acid-promoted disproportionation typical of nitronyl nitroxides.[14] The deprotonated carboxy group at position 5 of the pyrazole ring ($d_{C-O}$ = 1.249(2) and 1.252(2) Å) in the solid phase of **15**

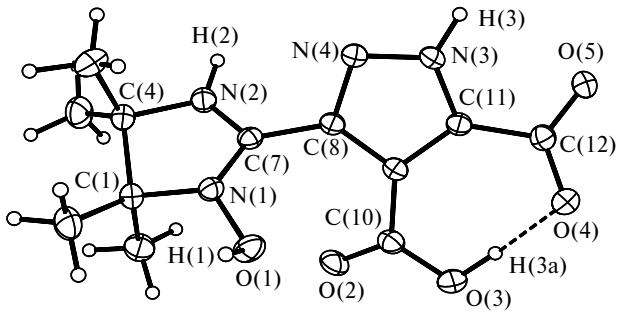
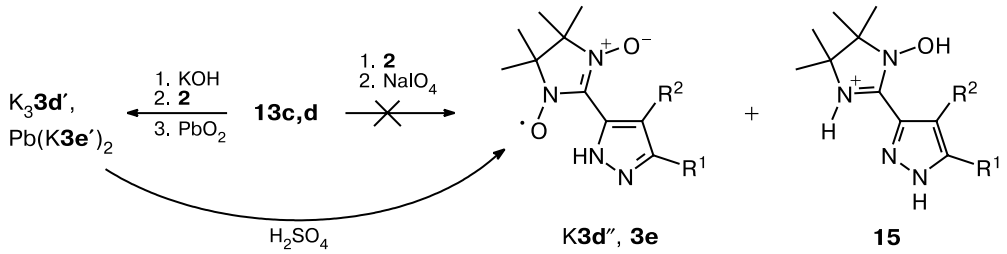



**Fig. 5.** Molecular structure of compound **15**.

**Scheme 6**




**3d′:** $R^1 = R^2 = CO_2^-$;
**3d″, 15:** $R^1 = CO_2^-$, $R^2 = CO_2H$;
**3e′:** $R^1 = CO_2^-$, $R^2 = H$;
**3e:** $R^1 = COOH$, $R^2 = H$

forms an intramolecular H bond with the carboxy group at position 4 ($d_{C=O}$ = 1.215(2), $d_{C-OH}$ = 1.311(2) Å). In addition, the O atoms of the carboxy groups are involved in hydrogen bonding with the protonated HO—N—C=N$^+$—H fragments ($d_{N-O}$, 1.375(2) Å; $d_{N-C}$, 1.312(2) and 1.322(2) Å) of the imidazolidine rings of the adjacent molecules, resulting in the formation of a framework structure.

Finely dispersed red-violet monopotassium salt K**3d″** was isolated from the mother liquor obtained after isolation of crystals of **15**. The magnetic moment $\mu_{eff}$ for K**3d″** (1.72 $\mu_B$ at 300 K) agrees well with the theoretical value for monoradicals (1.73 $\mu_B$). Treatment of an ethanolic solution of K**3d″** with an equivalent amount of $H_2SO_4$ led to the gradual disappearance of the red-violet color of the reaction mixture. The reaction mixture was concentrated, after which a yellow-brown residue was obtained. Washing of the latter with water followed by recrystallization from EtOH afforded a colorless product. Therefore, a spin-labeled dicarboxylic acid cannot be isolated according to this procedure.

Treatment of a methanolic solution of Pb(K**3e′**)$_2$ with an equivalent amount of sulfuric acid gave rise to acid **3e** in 40% yield (after purification) (see Scheme 6). Single crystals of acid **3e** were grown as the crystal hydrate **3e** · $H_2O$. Study of its structure demonstrated that the solid phase consists of ribbons stabilized by an extensive hydrogen bond network (Fig. 6). Since the O atom of only one NO group is involved in hydrogen bonding, $d_{N-O}$ in this group is slightly larger than that in another group (1.287(2) and 1.270(2) Å, respectively). High purity of the resulting acid is supported also by magnetic property measurements.

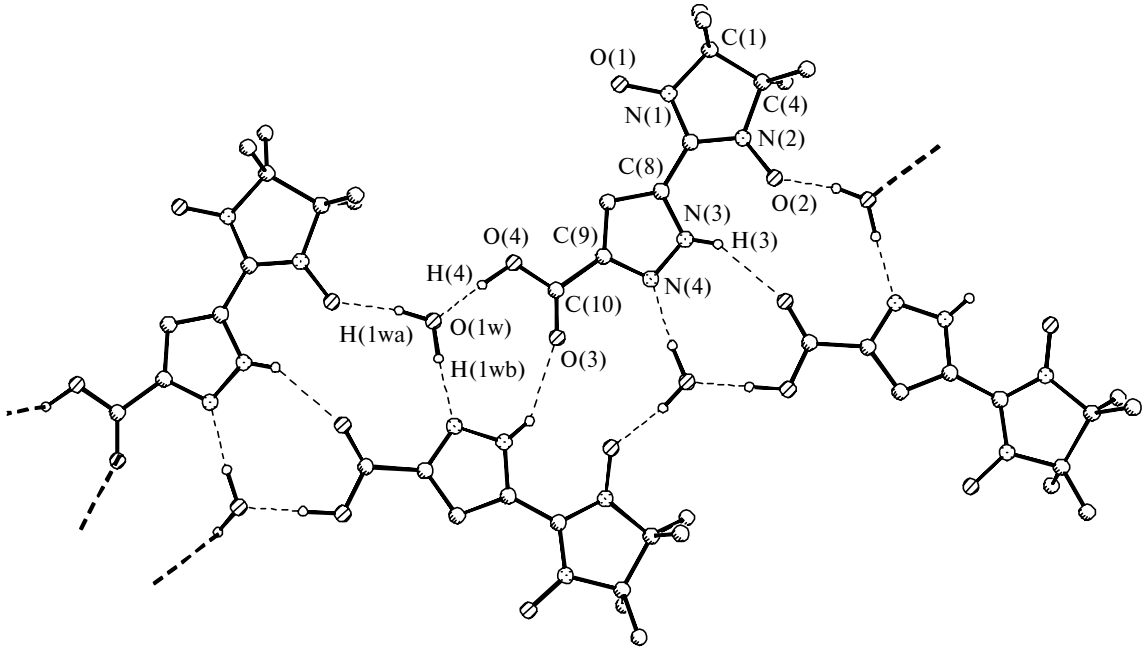
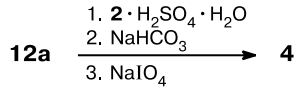



**Fig. 6.** Hydrogen bond network giving rise to polymeric ribbons in **3e** · $H_2O$ (the hydrogen atoms of the methyl groups are omitted).

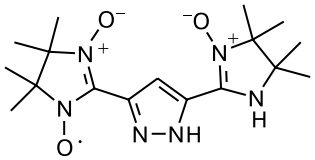
The magnetic moment $\mu_{eff}$ of (**3e**·$H_2O$) (1.734(2) $\mu_B$ in the temperature range of 77—300 K) is equal to the theoretical value (calculations based on the number of electrons) for free monoradicals ($g$ = 2.00) to within three decimal points.

Unlike acetals **12b,c**, compound **12a** has no ester groups, due to which it was directly used in the reaction with **2**·$H_2SO_4$·$H_2O$. After neutralization of the reaction mixture, $CHCl_3$ was added, and bis(dihydroxyimidazolidino)pyrazole that was present in the mixture was oxidized in the two-phase system with $NaIO_4$ to give bis(nitronyl nitroxide) **4** (Scheme 7).

**Scheme 7**




In this case, as in the above-described process with **3c**, the use of a **12a** : $NaIO_4$ molar ratio of 1 : 3 (*i.e.*, 1 : 1.5 with respect to one 1,3-dihydroxyimidazolidine (DHI) fragment) resulted in the rapid formation of a yellow-brown polymer-like mixture. A decrease in the **12a** : $NaIO_4$ ratio to 1 : 2 (*i.e.*, 1 : 1 with respect to one DHI fragment) led to the formation of a blue-green product, which can be separated into two individual compounds: biradical **4** (~17%) and a green product of unknown structure. The elemental analysis data are indicative of the presence of iodine in the latter product. Recrystallization of this product afforded a solid phase as X-ray amorphous green intergrown spherical particles. Only once, crystallization of this product from a mixture of $CH_2Cl_2$ and benzene during three weeks gave several small green crystals, which are (X-ray diffraction data) nitroxide **16**.



**16**

We found that the highest yield of **4** (47%) was achieved with the use of the **12a** : $NaIO_4$ molar ratio of 1 : 1.6 (or 1 : 0.8 with respect to one DHI fragment). Slow evaporation of a solution of bis(nitronyl nitroxide) **4** from a $CH_2Cl_2$—heptane mixture afforded well-faceted dark-blue crystals. The structure of the dimeric molecules is shown in Fig. 7. The magnetic moment $\mu_{eff}$ for **4** (2.41 $\mu_B$ at 77—300 K) agrees well with the theoretical value for biradicals (2.45 $\mu_B$).

To summarize, we demonstrated that the approach to the synthesis of pyrazole-substituted nitronyl nitroxides

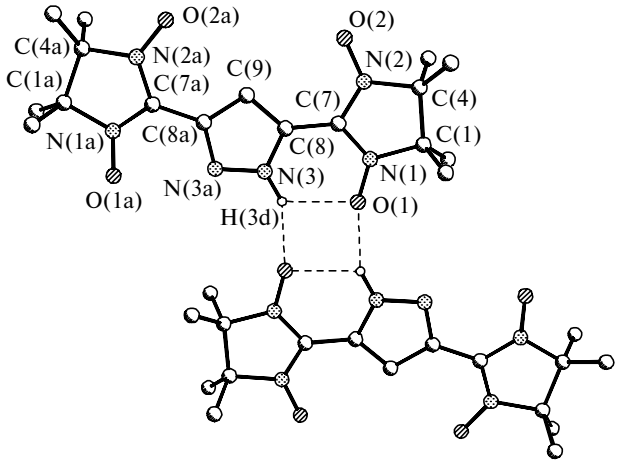



**Fig. 7.** Mode of dimerization of molecules **4** (the hydrogen atoms of the methyl groups are omitted).

based on the initial preparation of the required pyrazole derivatives by 1,3-dipolar addition is rather efficient and allows the synthesis of a wide range of polyfunctional nitroxides. The use of 1,3-dipolar addition as the initial step of the synthesis made it possible to prepare the previously inaccessible mononitronyl nitroxides **3b—e** and bis(nitronyl nitroxide) **4**, whose structures were confirmed by X-ray diffraction study.

## Experimental

The course of the reactions was monitored by TLC on Aluminum oxide on aluminum sheets, 60 $F_{254}$ neutral, and Silica gel 60 $F_{254}$ aluminum sheets (Merck). Column chromatography was carried out on silica gel (0.063—0.200 mm; Merck) and $Al_2O_3$ (chromatographic grade) purchased from the Donetsk Plant of Chemical Reagents. The IR spectra were recorded in the 400—4000 $cm^{-1}$ region on a VECTOR-22 Bruker spectrophotometer (KBr pellets). The melting points were determined on a Boetius microheating table. Microanalyses were performed on a Carlo Erba 1106 analyzer at the Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The mass spectra were obtained on a Finnigan MAT-8200 mass spectrometer (electron impact ionization, 70 eV). The molecular weights of the anions in the salts $Pb_3O_2$(**3b**′)$_2$, $K_3$**3d**′·$2H_2O$, Pb(K**3e**′)$_2$·3MeOH, and K**3d″** were determined using a mass-selective detector (G1946C, Agilent 1100 Serie LC/MSD), which was used in electrostatic spray mode (API-AS); the negative ions were scanned in the $m/z$ range from 100 to 1000. The NMR spectra were recorded on a Bruker Avance 300 spectrometer at room temperature (23—26 °C) using the signal of the solvent as the internal standard ($\delta_H$ = 7.24 for $CDCl_3$ and $\delta_H$ = 2.05 for acetone-$d_6$). The magnetic measurements were performed on a SQUID MPMS-5S (Quantum Desing) magnetometer in the temperature range of 2—300 K at 5 kOe.

Dimethyl sulfate-$d_6$ (>99%, Aldrich), NaH (60% in mineral oil), DMF (99.8%, Aldrich), and $NaIO_4$ (>99.5%, Fluka) were used without additional purification. 2,3-Bis(hydroxyamino)-

2,3-dimethylbutane (**2**), its sulfate hydrate $\mathbf{2}\cdot H_2SO_4\cdot H_2O$,[15,16] 3,3-diethoxyprop-1-yne,[17] and 1-methyl-1-nitrosourea[18] were synthesized according to known procedures. The reagent $C_2D_5I$ was prepared from anhydrous $C_2D_5OD$ according to a procedure developed for the synthesis of $C_2H_5I$.[19] The Pb content in the complexes was determined by chelate titration with Eriochrome Black T as the indicator.[20]

**1-(2,2-Dimethoxyethyl)urea** was synthesized according to two methods (*A* and *B*). *A*. 1-(2,2-Dimethoxyethyl)urea[21] was prepared from 2,2-dimethoxyethylamine (12 g, 0.11 mol) and KOCN (10 g, 0.12 mol) in a yield of 16 g (98%). *B*. A mixture of urea (12.2 g, 0.2 mol) and 2,2-dimethoxyethylamine (21.4 g, 0.2 mol) was heated to 140—150 °C and stirred at this temperature for 6 h. Elimination of ammonia started at 100 °C and occurred extensively during the first hour. The reaction mixture was cooled, and $Et_2O$ (~100 mL) was added to the resulting viscous pale-yellow oil. Trituration of the product caused its crystallization. The finely dispersed white precipitate was filtered off. The mother liquor was concentrated and stored in a refrigerator, after which an additional amount of crystals was obtained. The total yield was 23.4 g (78%), m.p. 55—56 °C (hexane—AcOEt). IR, ν/cm$^{-1}$: 726, 832, 885, 1067, 1311, 1364, 1435, 1656, 2936, 3442. $^1$H NMR ($CDCl_3$), δ: 3.34 (d, 2 H, $CH_2$, $J$ = 7.0 Hz); 3.43 (s, 6 H, $(OCH_3)_2$); 4.2 (br.s, NH); 4.41 (t, 1 H, CH, $J$ = 7.0 Hz); 5.1 (br.s, $NH_2$).

**1-(2,2-Dimethoxyethyl)-1-nitrosourea** was synthesized analogously to 1-(2,2-diethoxyethyl)-1-nitrosourea[22], m.p. 63—64 °C (hexane). IR, ν/cm$^{-1}$: 697, 775, 814, 867, 943, 1009, 1062, 1129, 1206, 1295, 1421, 1484, 1607, 1738, 2841, 2946, 3401. $^1$H NMR ($CDCl_3$), δ: 3.30 (s, 6 H, $(OCH_3)_2$); 3.98 (d, 2 H, $CH_2$, $J$ = 7.0 Hz); 4.51 (t, 1 H, CH, $J$ = 7.0 Hz); 5.60 and 6.80 (both br.s, 1 H each, NH). Found (%): C, 34.1; H, 6.2; N, 23.7. $C_5H_{11}N_3O_4$. Calculated (%): C, 33.9; H, 6.3; N, 23.7.

**2,2-Dimethoxydiazoethane** was synthesized analogously to 2,2-diethoxy-1-diazoethane.[22,23]

**4,4,5,5-Tetramethyl-2-(1*H*-pyrazol-4-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (1a, R = H) and 4,4,5,5-tetramethyl-2-(1*H*-pyrazol-3-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (3a, R$^1$ = R$^2$ = H).** 1-Methyl-1-nitrosourea (14.4 g, 0.14 mol) was added portionwise to an ice-cooled mixture of a 40% aqueous KOH solution (60 g) and $Et_2O$ (100 mL) for 1 h. After the addition of each portion of 1-methyl-1-nitrosourea, the reaction mixture was shaken manually for about 1 min. The resulting solution of diazomethane in $Et_2O$ (*CAUTION! Diazomethane is a highly toxic compound irritating mucous membranes. In addition, it readily detonates. Hence, special precautions should be taken, such as specially chosen glassware, a protecting screen, etc.*) was decanted into an ice-cooled flat-bottomed vessel containing 3,3-diethoxyprop-1-yne (**5**) (5.0 g, 6.1 mL, 0.039 mol). The reaction mixture was kept at ~20 °C for 4 days, after which it became completely colorless. Diethyl ether was distilled off under standard pressure, and alkyne **5** was distilled off *in vacuo* at 15 Torr and a bath temperature of 50 °C. An yellow oil containing acetal **6** was obtained in a yield of 6.06 g. The independent synthesis afforded the oil in a yield of 6.72 g.

The compound $\mathbf{2}\cdot H_2SO_4\cdot H_2O$ (21.0 g, 0.080 mol) was added with stirring into a 300 mL beaker containing a mixture of the oil prepared in the previous step (12.8 g) and water (40 mL). The solution was stirred for 5 h during which it gradually became viscous. The yellow cream-like substance was carefully neutralized with $NaHCO_3$ (18 g). The resulting sticky substance was transferred to a filter, pressed, and suspended in acetone (200 mL). The insoluble precipitate was filtered off and dried in air, and to prepare a pale-yellow powder containing imidazolidines **8** and **9** (28 g), which were oxidized without additional purification.

Sodium periodate (13 g, 0.06 mol) was added portionwise to a stirred solution of the powder (28 g) prepared in the previous step in a mixture of $CHCl_3$ (100 mL) and $H_2O$ (50 mL) at 3—5 °C for 30 min. The reaction mixture was filtered off, the organic phase was separated, and the aqueous phase was additionally treated with $CHCl_3$ (4×20 mL). The combined organic extracts were dried with $Na_2SO_4$, the solvent was distilled off, and the residue was chromatographed on an $Al_2O_3$ column (25×2 cm). Chloroform was used as the first eluent until nitroxide **1a** appeared in the eluate. Then the column was eluted with EtOH, and the fraction containing **1a** was collected. The ethanol fraction was concentrated, and the residue was recrystallized from a $CH_2Cl_2$—benzene mixture. The chloroform fraction was concentrated, and the residue was dissolved in hot benzene (~30 mL) and applied onto a silica gel column (25×2 cm) eluted with $CHCl_3$, an orange fraction containing nitroxide **10** being eluted first, after which a blue fraction containing nitroxide **3a** was eluted.

Compound **1a**. The yield was 4.4 g (25% with respect to 10 g of 3,3-diethoxypropyne **5**), blue crystals, $R_f$ ($Al_2O_3$, AcOEt) 0.19, $R_f$ 0.25 (silica gel, AcOEt) 0.25, m.p. 192—192.5 °C (from a benzene—hexane mixture); $\mu_{eff}$ = 1.72 $\mu_B$ (300 K). IR, ν/cm$^{-1}$: 662, 670, 749, 809, 868, 899, 938, 961, 995, 1041, 1127, 1154, 1172, 1216, 1283, 1313, 1342, 1369, 1396, 1409, 1434, 1458, 1520, 1608, 2989, 3119, 3200. Found (%): C, 53.9; H, 6.7; N, 25.2. $C_{10}H_{15}N_4O_2$. Calculated (%): C, 53.8; H, 6.8; N, 25.1.

Compound **3a**. The yield was 0.56 g (6.4% with respect to 10 g of **5**), blue-violet crystals, $R_f$ 0.30 ($Al_2O_3$, AcOEt), $R_f$ (silica gel, AcOEt) 0.44, m.p. 148—149 °C (from a benzene—hexane mixture); $\mu_{eff}$ = 1.73 $\mu_B$ (300 K). IR, ν/cm$^{-1}$: 765, 817, 870, 901, 921, 1016, 1037, 1098, 1137, 1190, 1210, 1242, 1270, 1299, 1374, 1406, 1428, 1453, 1494, 2992, 3283 br. Found (%): C, 53.9; H, 6.5; N, 24.8. $C_{10}H_{15}N_4O_2$. Calculated (%): C, 53.8; H, 6.8; N, 25.1.

**4,4,5,5-Tetramethyl-2-(1*H*-pyrazol-3-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl (10).** A mixture of **3a** (250 mg, 1.12 mmol), $NaNO_2$ (150 mg, 2.17 mmol), $CHCl_3$ (15 mL), HOAc (0.2 mL), and $H_2O$ (0.2 mL) was stirred at 40—45 °C until the starting nitronyl nitroxide was consumed (2 h). The cooled reaction mixture was neutralized with $NaHCO_3$, dried with $Na_2SO_4$, and filtered through a layer of $Al_2O_3$. The solvent was distilled off, the residue was chromatographed on an $Al_2O_3$ column (25×2 cm) eluted with benzene, and an orange fraction was collected. The yield was 120 mg (52%), red needle-like crystals, m.p. 151—152 °C (from a benzene—hexane mixture); $\mu_{eff}$ = 1.73 $\mu_B$ (300 K). IR, ν/cm$^{-1}$: 561, 602, 624, 721, 781, 829, 857, 881, 920, 1053, 1097, 1147, 1169, 1221, 1249, 1269, 1289, 1353, 1369, 1422, 1463, 1481, 1546, 1591, 2941, 3047, 3149 br. Found (%): C, 58.2; H, 7.4; N, 26.9. $C_{10}H_{15}N_4O$. Calculated (%): C, 58.0; H, 7.3; N, 27.0.

**4,4,5,5-Tetramethyl-2-(1-trideuteriomethyl-1*H*-pyrazol-4-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (1c).** Sodium hydride (60% in mineral oil, 60 mg, 1.5 mmol) was added to a stirred solution of nitroxide **2a** (330 mg, 1.5 mmol) in DMF (6 mL) at room temperature under argon. The reaction mixture was stirred for 20 min, dimethyl sulfate-$d_6$ (150 μL, 200 mg,

1.5 mmol) was added, and the reaction mixture was stirred for 30 min. The solvent was distilled off at a bath temperature of ~60 °C, $CHCl_3$ (20 mL) was added to the residue, the solution was filtered through a layer of silica gel (1.5×6 cm), and the product was eluted with ethyl acetate. The blue fraction was concentrated, and the residue was chromatographed on an $Al_2O_3$ column (1.5×20 cm) eluted with $CHCl_3$. The product was recrystallized from a 1 : 1 benzene—hexane mixture. The yield was 310 mg (86%), m.p. 174—175 °C (from a 1 : 1 benzene—heptane mixture); $\mu_{eff} = 1.72\ \mu_B$ (300 K). IR, ν/cm$^{-1}$: 543, 664, 754, 814, 832, 865, 984, 1017, 1078, 1136, 1180, 1224, 1317, 1347, 1371, 1397, 1428, 1456, 1481, 1600, 2076, 2122, 2162, 2980, 3147. High-resolution MS. Found: *m/z* = 240.1576 $[M]^+$. $C_{11}H_{14}D_3N_4O_2$. Calculated: M = 240.1540. MS, *m/z* ($I_{rel}$ (%)): 241 $[M+1]^+$ (12), 240 $[M]^+$ (100), 178 (10), 112 (52), 111 (22), 84 (40), 83 (16), 69 (59), 56 (71), 55 (30). Found (%): C, 55.1; H+D, 7.1; N, 23.3. $C_{11}H_{14}D_3N_4O_2$. Calculated (%): C, 55.0; H+D, 7.1; N, 23.3.

**4,4,5,5-Tetramethyl-2-(1-pentadeuterioethyl-1*H*-pyrazol-4-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (1d)** was synthesized analogously with the use of iodoethane-$d_5$ (130 μL, 240 mg, 1.5 mmol). After completion of the synthesis and removal of the solvent, $C_6H_6$ (20 mL) was added to the residue. The solution was filtered and concentrated. The yield was 320 mg (83%), m.p. 100—103 °C, $\mu_{eff} = 1.73\ \mu_B$ (300 K). IR, ν/cm$^{-1}$: 542, 665, 866, 985, 1018, 1140, 1181, 1223, 1315, 1347, 1399, 1428, 1451, 1601, 2075, 2124, 2141, 2169, 2233, 2872, 2931, 2979, 3002, 3145. MS, *m/z* ($I_{rel}$ (%)): 257 $[M + 1]^+$ (9), 256 $[M]^+$ (69), 168 (14), 128 (38), 127 (33), 114 (13), 96 (12), 95 (13), 94 (11), 84 (92), 83 (14), 69 (83), 56 (100). Found (%): C, 56.4; H+D, 7.8; N, 22.0. $C_{12}H_{14}D_5N_4O_2$. Calculated (%): C, 56.2; H+D, 7.6; N, 21.9.

**2-(1-Carbamoylmethyl-1*H*-pyrazol-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (1e)** was synthesized analogously. The yield was 54 mg (71%), m.p. 206—208 °C (from toluene), $\mu_{eff} = 1.72\ \mu_B$ (300 K). IR, ν/cm$^{-1}$: 540, 618, 792, 820, 839, 868, 896, 964, 1005, 1127, 1172, 1202, 1320, 1353, 1408, 1435, 1461, 1484, 1606, 1682, 2937, 2988, 3193, 3382. High-resolution MS. Found: *m/z* 280.1409 $[M]^+$. $C_{12}H_{18}N_5O_3$. Calculated: M = 280.1410. MS, *m/z* ($I_{rel}$ (%)): 281 $[M + 1]^+$ (13), 280 $[M]^+$ (89), 152 (35), 151 (16), 106 (11), 84 (95), 83 (20), 69 (96), 56 (100). Found (%): C, 50.2; H, 6.4; N, 24.2. $C_{12}H_{18}N_5O_3 \cdot 0.5H_2O$. Calculated (%): C, 49.8; H, 6.6; N, 24.2.

**3-(Dimethoxymethyl)-1*H*-pyrazole-5-carbaldehyde (12a).** Acetal **5** (2.15 g, 2.4 mL, 16.8 mmol) was added with stirring to a mixture of 0.2 *N* $H_2SO_4$ (4 mL) and hydroquinone (8 mg) at 80 °C. Propiolaldehyde that formed was distilled off through a descending condenser into a stirred solution of 2,2-dimethoxydiazoethane in diethyl ether (~50 mL), which was prepared from 1-(2,2-dimethoxyethyl)-1-nitrosourea (1.5 g, 8.5 mmol). The starting bright-yellow reaction mixture gradually turned pale-pink. After completion of the addition of propiolaldehyde, the reaction mixture was stirred for 20 min and concentrated. The residue was triturated with hexane on cooling, and the creamy-colored precipitate was filtered off. The yield was 1.18 g (82%), m.p. 128—131 °C. IR, ν/cm$^{-1}$: 858, 915, 982, 1022, 1060, 1102, 1141, 1178, 1194, 1222, 1290, 1334, 1362, 1401, 1447, 1474, 2835, 2905, 2968, 3146 br. Found (%): C, 49.5; H, 6.0; N, 16.2. $C_7H_{10}N_2O_3$. Calculated (%): C, 49.4; H, 5.9; N, 16.5.

**Diethyl 3-formyl-1*H*-pyrazole-4,5-dicarboxylate (13a).** A solution of 2,2-dimethoxydiazoethane in diethyl ether, which was prepared from 1-(2,2-dimethoxyethyl)-1-nitrosourea (7.0 g, 40 mmol), was added dropwise to a stirred solution of diethyl acetylenedicarboxylate (4.8 g, 28 mmol) in diethyl ether (20 mL) at 0 °C. The solvent was distilled off *in vacuo*, $HCO_2H$ (11 mL) was added to the oily residue (10.4 g), and the mixture was stirred for 6 h. The white precipitate that formed was filtered off and washed with diethyl ether. The yield was 4.16 g (50%), m.p. 139—144 °C. IR, ν/cm$^{-1}$: 615, 756, 873, 950, 1022, 1087, 1157, 1200, 1227, 1320, 1369, 1410, 1452, 1492, 1547, 1703, 1739, 2980, 3311. Found (%): C, 49.9; H, 5.1; N, 11.5. $C_{10}H_{12}N_2O_5$. Calculated (%): C, 50.0; H, 5.0; N, 11.7.

**Ethyl 3-formyl-1*H*-pyrazole-5-carboxylate (13b).** Ethyl propiolate (1.9 mL, 19 mmol) was added to an yellow solution of 2,2-dimethoxydiazoethane in diethyl ether, which was prepared from 1-(2,2-dimethoxyethyl)-1-nitrosourea (2.66 g, 15 mmol). The reaction mixture was refluxed with stirring for 30 min, during which it gradually turned colorless. The solvent was distilled off *in vacuo*, $HCO_2H$ (3.3 mL) was added to the oily residue (3.23 g), and the solution was stirred for 1 h. The finely dispersed pale-yellow precipitate that formed was filtered off and washed with diethyl ether. The yield was 1.50 g (60%), m.p. 136—138 °C. IR, ν/cm$^{-1}$: 780, 819, 841, 897, 995, 1034, 1065, 1104, 1173, 1205, 1242, 1295, 1365, 1385, 1457, 1724, 1743, 2984, 3184. $^1$H NMR (acetone-$d_6$), δ: 1.36 (t, 3 H, Me, *J* = 7.0 Hz); 4.38 (κ, 2 H, $CH_2$, *J* = 7.0 Hz); 7.27 (br.s, 1 H, C—$H_{Pyr}$); 9.98 (s, 1 H, CHO). Found (%): C, 50.1; H, 4.8; N, 16.6. $C_7H_8N_2O_3$. Calculated (%): C, 50.0; H, 4.8; N, 16.7.

**3-Formyl-1*H*-pyrazole-4,5-dicarboxylic acid (13c).** A 10% aqueous NaOH solution (20 mL) was added with stirring to a suspension of **13a** (2.0 g, 8.3 mmol) in MeOH (2 mL). The resulting pale-yellow solution was stirred for 6 h, and a concentrated aqueous HCl solution was added dropwise to pH ~3. After 15 min, the finely dispersed white precipitate that formed was filtered off, washed with a weak aqueous HCl solution, pH 3, and dried in air. The yield was 1.38 g (90%). IR, ν/cm$^{-1}$: 784, 864, 947, 1066, 1124, 1171, 1229, 1301, 1328, 1476, 1559, 1591, 2758, 2872, 3355, 3606. Satisfactory results of elemental analysis were not obtained because **13c** is very poorly soluble and is prone to decarboxylation on heating. Found (%): C, 27.0; H, 2.0; N, 10.0. The C : N ratio was 2.7. $C_6H_4N_2O_5$. Calculated (%): C, 39.1; H, 2.2; N, 15.2. The C : N ratio was 2.6. Compound **13c** was used without additional purification.

**3-Formyl-1*H*-pyrazole-5-carboxylic acid (13d).** A 5% aqueous NaOH solution (18 mL) was added to a stirred suspension of **13b** (0.8 g, 4.8 mmol) in MeOH (5 mL). After 4 h, concentrated HCl was added dropwise to the solution to pH ~0. The white precipitate that formed was filtered off, washed with a weak aqueous HCl solution, pH 3, and dried in air. The yield was 0.60 g (90%). IR, ν/cm$^{-1}$: 768, 782, 821, 843, 900, 1009, 1076, 1110, 1172, 1218, 1272, 1399, 1453, 1495, 1548, 1706, 2608, 2758, 3158. High-resolution MS. Found: *m/z* 140.0210 $[M]^+$. $C_5H_4N_2O_3$. Calculated: M = 140.0222. MS, *m/z* ($I_{rel}$ (%)): 141 $[M + 1]^+$ (6.7), 140 $[M]^+$ (100), 139 $[M - H]$ (33), 121 $[M - H_2O]$ (59), 112 $[M - CO]$ (41), 96 (14). Found (%): C, 42.0; H, 2.8; N, 19.0. $C_5H_4N_2O_3$. Calculated (%): C, 42.9; H, 2.9; N, 20.0.

**Diethyl 3-(1,3-dihydroxy-4,4,5,5-tetramethylimidazolidin-2-yl)-1*H*-pyrazole-4,5-dicarboxylate (14a).** A solution of aldehyde **13a** (2.0 g, 8.3 mmol) and **2** (1.23 g, 8.3 mmol) in methanol

(40 mL) was stirred for 5 h. Then the solvent was distilled off. The pale-yellow oily product was dissolved in a minimum amount of diethyl ether, hexane was added, and the reaction mixture was kept at ~0 °C for several days. The product was initially obtained as an oil, which gradually crystallized. The colorless crystals were filtered off, the yield was 3.0 g (98%), m.p. 114—118 °C. IR, ν/cm$^{-1}$: 579, 770, 812, 862, 1019, 1091, 1161, 1223, 1296, 1368, 1469, 1703, 1724, 2983, 3287, 3448. $^1$H NMR (acetone-$d_6$), δ: 1.13 (s, 6 H, C(CH$_3$)$_2$); 1.17 (s, 6 H, C(CH$_3$)$_2$); 1.31 and 1.33 (both t, 3 H each, C(4)CO$_2$CH$_2$C<u>H</u>$_3$, C(5)CO$_2$CH$_2$C<u>H</u>$_3$, $J$ = 7.1 Hz); 4.23 and 4.31 (both q, 2 H each, C(4)CO$_2$CH$_2$, C(5)CO$_2$CH$_2$, $J$ = 7.1 Hz); 5.41 (s, 1 H, H(2′)); 7.2 (br.s, 1.6 H). Found (%): C, 52.2; H, 7.2; N, 15.3. $C_{16}H_{26}N_4O_6$. Calculated (%): C, 51.9; H, 7.1; N, 15.1.

**Ethyl 3-(1,3-dihydroxy-4,4,5,5-tetramethylimidazolidin-2-yl)-1*H*-pyrazole-5-carboxylate (14b).** Compound **2** (0.45 g, 3 mmol) was added to a solution of aldehyde **13b** (0.5 g, 3 mmol) in methanol (10 mL), and the reaction mixture was stirred for 3 h. The solvent was distilled off, the resulting oil was dissolved in a minimum amount of ethyl acetate, and benzene was added. Then the solution was cooled and ground with a rod, which gave rise to a finely dispersed white precipitate. The latter was filtered off and washed on a filter with hexane. The yield was 0.58 g (65%), m.p. 140—143 °C. IR, ν/cm$^{-1}$: 779, 849, 996, 1025, 1180, 1240, 1265, 1299, 1337, 1373, 1387, 1411, 1444, 1465, 1710, 2932, 2985, 3137, 3294, 3388. Found (%): C, 49.6; H, 8.0; N, 17.6. $C_{13}H_{22}N_4O_4 \cdot H_2O$. Calculated (%): C, 49.4; H, 7.7; N, 17.7.

**Diethyl 3-(4,4,5,5-tetramethyl-3-oxido-1-oxyl-4,5-dihydro-1*H*-imidazol-2-yl)-1*H*-pyrazole-4,5-dicarboxylate (3b).** Sodium periodate (1.6 g, 7.5 mmol) was added portionwise to a stirred mixture of **14a** (1.8 g, 5 mmol), chloroform (40 mL), and water (10 mL) for 5 min. The formation of a white substance in the aqueous phase was observed, and the organic phase turned pale-blue. The poorly soluble compound gradually disappeared in the course of stirring of the reaction mixture for 1.5 h, and the chloroform layer turned bright-blue. The organic layer was separated, and the aqueous phase was extracted with chloroform (2×5 mL). The combined organic solutions were dried with $Na_2SO_4$ and filtered through a layer of silica gel (1.5×3 cm). The solvent was removed, and the oily dark-blue residue was dissolved in a mixture of hexane and benzene. The solution was decanted, the gray-green by-product remaining on the walls of the flask. Then the solution was applied onto a silica gel column (1.5×15 cm) eluted with $CHCl_3$, and a blue-violet fraction was collected. The latter was concentrated, and an oil was obained in a yield of 1.90 g. The oil was kept *in vacuo* at 40 °C for 16 h. Compound **3b** was obtained as a dark-blue oil in a yield of 1.50 g (82%). IR, ν/cm$^{-1}$: 540, 773, 847, 1036, 1096, 1171, 1219, 1292, 1372, 1415, 1449, 1633, 1727, 2934, 2986, 3453. High-resolution MS. Found: $m/z$ 367.1623 [M]$^+$. $C_{16}H_{23}N_4O_6$. Calculated: M = 367.1618. MS, $m/z$ ($I_{rel}$ (%)): 367 (2) 250 (16), 164 (12), 84 (100), 69 (30), 56 (17). Found (%): C, 51.7; H, 6.4; N, 14.7. $C_{16}H_{23}N_4O_6$. Calculated (%): C, 52.3; H, 6.3; N, 15.3.

**Complex $Pb_3O_2(3b')_2$ (3b′ is deprotonated 3b).** Lead oxide (1 g, 4.2 mmol) was added to a solution of **14a** (0.5 g, 1.4 mmol) in methanol (5 mL). The reaction mixture was stirred for 2 h and filtered. The solution was concentrated, and the oily dark-blue residue was triturated with a mixture of hexane and ethyl acetate, resulting in crystallization. The precipitate was filtered off, washed with hexane, and dried in air. The yield was 0.2 g. The compound decomposes at ~220—230 °C, is poorly soluble in $H_2O$, AcOEt, toluene, and diethyl ether, and is readily soluble

**Table 1.** Principal crystallographic data and details of X-ray diffraction studies

| Parameter | 1a | 1c | 1d | 3a |
|---|---|---|---|---|
| Space group | $P\bar{1}$ | $P2_1/n$ | $P2_1/n$ | $C2/c$ |
| $a$/Å | 7.1757(15) | 9.6638(11) | 9.8305(16) | 23.522(4) |
| $b$/Å | 13.026(3) | 11.4304(12) | 11.6094(19) | 7.8792(13) |
| $c$/Å | 14.057(3) | 11.7101(13) | 11.979(2) | 12.417(2) |
| α/deg | 63.902(4) | | | |
| β/deg | 80.129(4) | 108.214(2) | 105.223(3) | 101.013(4) |
| γ/deg | 86.402(4) | | | |
| $V$/Å | 1162.4(4) | 1228.7(2) | 1319.1(4) | 2259.0(7) |
| $Z$ | 4 | 4 | 4 | 8 |
| $d_{calc}$/g cm$^{-3}$ | 1.276 | 1.299 | 1.291 | 1.313 |
| μ/mm$^{-1}$ | 0.094 | 0.091 | 0.089 | 0.095 |
| θ Scan range/deg | 1.74—23.25 | 2.39—23.28 | 2.39—23.27 | 2.73—23.30 |
| Number of measured reflections | 5593 | 8698 | 5196 | 4741 |
| Number of independent reflections | 1895 | 3315 | 1756 | 1637 |
| $R_{int}$ | 0.0682 | 0.0316 | 0.0555 | 0.0559 |
| Reflections with $I > 2\sigma(I)$ | 2158 | 1307 | 1682 | 1064 |
| Number of parameters in refinement | 392 | 223 | 240 | 206 |
| $R$ factors ($I > 2\sigma$) | | | | |
| $R_1$ | 0.0496 | 0.0373 | 0.0403 | 0.0493 |
| $wR_2$ | 0.1072 | 0.1021 | 0.1149 | 0.1226 |
| $R$ factors (all reflections) | | | | |
| $R_1$ | 0.0780 | 0.0537 | 0.0506 | 0.0799 |
| $wR_2$ | 0.1196 | 0.1138 | 0.1246 | 0.1426 |
| GOOF | 0.857 | 0.740 | 0.878 | 0.785 |

in $CH_2Cl_2$, acetone, MeOH, and EtOH. Crystallization of $Pb_3O_2(\mathbf{3b}')_2$ from $CH_2Cl_2$—heptane, $CH_2Cl_2$—AcOEt, and acetone—toluene solvent mixtures afforded a finely dispersed blue powder. Recrystallization of $Pb_3O_2(\mathbf{3b}')_2$ from a MeOH—$H_2O$ mixture gave a black-blue film on the bottom of the flask, and the film cracked during drying in air. The fingerprint regions of the IR spectra of the samples obtained by crystallization from different solvents are identical. IR, ν/cm$^{-1}$: 775, 850, 874, 1050, 1098, 1138, 1169, 1215, 1249, 1298, 1337, 1370, 1396, 1461, 1515, 1571, 1721, 2936, 3283, 3436. MS, *m/z* ($I_{rel}$ (%)): 367 [**3b**′ + 1]$^-$ (7), 366 [**3b**′]$^-$ (47), 352 (100), 336 (77). Found (%): C, 27.5; H, 2.9; N, 8.4; Pb, 42.2. $C_{32}H_{44}N_8O_{14}Pb_3$. Calculated (%): C, 27.7; H, 3.2; N, 8.1; Pb, 44.9.

**Complex Ni(3b′)$_2$·2H$_2$O.** Nickel sesquioxide $Ni_2O_3$ (1.25 g, 7.6 mmol) was added to a solution of **14a** (0.33 g, 0.89 mmol) in methanol (5 mL). The reaction mixture was stirred at ~20 °C for two days and filtered. The solution was concentrated *in vacuo*, the residue was dissolved in MeOH (10 mL), and $H_2O$ (10 mL) was added. The solution was kept in an open flask in a thermostat at 20 °C. After 1 day, the gray precipitate that formed was filtered off, the filtrate was concentrated, and the blue residue was triturated with a mixture of hexane and benzene, resulting in the formation of a blue powder, which was filtered off, washed with diethyl ether, and recrystallized from a mixture of MeOH and water. The yield was 0.2 g (53%). The complex is poorly soluble in water and diethyl ether and is readily soluble in methanol and ethanol. IR, ν/cm$^{-1}$: 775, 853, 878, 1050, 1097, 1140, 1170, 1217, 1286, 1370, 1392, 1461, 1511, 1622, 1728, 2981, 3435 br. Found (%): C, 46.4; H, 5.9; N, 14.0. $C_{32}H_{44}N_8NiO_{12}\cdot 2H_2O$. Calculated (%): C, 46.5; H, 5.9; N, 13.5.

**Ethyl 3-(4,4,5,5-tetramethyl-3-oxido-1-oxyl-4,5-dihydro-1*H*-imidazol-2-yl)-1*H*-pyrazole-5-carboxylate (3c).** Sodium periodate (0.12 g, 0.6 mmol) was added portionwise to a stirred mixture of dihydroxyimidazolidine **14b** (0.3 g, 1 mmol), $CHCl_3$ (6 mL), and $H_2O$ (4 mL) at room temperature for 5 min. A poorly soluble white compound was accumulated in the aqueous phase, and the organic phase turned blue-green. The poorly soluble compound disappeared after stirring of the reaction mixture for 1 h, and the chloroform layer turned bright-blue. The organic layer was separated and the aqueous phase was extracted with chloroform (1×5 mL). The combined organic solutions were dried with $Na_2SO_4$. The solvent was removed on a rotary evaporator, and the residue was crystallized by trituration with hexane. The yield was 0.28 g (94%), m.p. 166—171 °C; $\mu_{eff}$ = 1.73 $\mu_B$ (300 K). IR, ν/cm$^{-1}$: 779, 837, 868, 985, 1025, 1089, 1157, 1227, 1260, 1369, 1395, 1460, 1730, 2994, 3227. Found (%): C, 52.8; H, 6.4; N, 18.9. $C_{13}H_{19}N_4O_4$. Calculated (%): C, 52.9; H, 6.5; N, 19.0.

**Complex Pb(K3e′)$_2$·3MeOH.** Compound **13d** (0.5 g, 3.6 mmol) was added to a stirred solution of KOH (0.2 g, 3.6 mmol) in MeOH (9 mL). After 10 min, compound **2** (0.53 g, 3.6 mmol) was added. After 1 day, the reaction mixture (a pale-yellow suspension) was filtered, $PbO_2$ (4.5 g, 18.8 mmol) was added to the filtrate, and the mixture was stirred for one day and filtered. The solvent was removed, THF (25 mL) was added to the bright-blue residue, and the mixture was heated to 50 °C and filtered. The filtrate was concentrated, the residue was dissolved in MeOH (10 mL), toluene (5 mL) was carefully added along the wall of the flask, and the mixture was kept in an open flask at room temperature. The black-blue precipitate that formed was filtered off and washed with hexane. The yield was 1.03 g; $\mu_{eff}$ = 2.35 $\mu_B$ (300 K). IR, ν/cm$^{-1}$: 803, 898, 1018, 1045, 1166, 1212, 1352, 1452, 1581, 2983, 3405. MS, *m/z* ($I_{rel}$ (%)): 487 (5), 437 (6), 376 (10), 306 (31), 291 (63), 267 [**3e**′ + H$^+$ + 1]$^-$ (9), 266

| **3c** | **3e**·$H_2O$ | **4** | **10** | **14a** | **15** | **16**·$C_7H_8$ |
|---|---|---|---|---|---|---|
| $P2_1/c$ | $P2_1/n$ | $P2_1/c$ | $P2_1/c$ | $P2_12_12_1$ | $P2_1/n$ | $C2/c$ |
| 10.188(5) | 8.9902(10) | 13.173(5) | 12.531(6) | 11.018(2) | 7.237(16) | 25.498(8) |
| 6.781(3) | 11.5567(13) | 12.041(4) | 9.317(4) | 23.499(5) | 14.765(3) | 9.129(3) |
| 21.993(10) | 14.0991(15) | 12.879(4) | 10.260(4) | 7.4085(15) | 12.938(3) | 22.635(6) |
| 102.340(10) | 99.111(2) | 110.972(7) | 111.678(10) | — | 93.541(3) | 106.721(8) |
| 1484.2(11) | 1446.4(3) | 1907.6(11) | 1113.2(8) | 1918.2(7) | 1379.9(5) | 5046.0(2) |
| 4 | 4 | 4 | 4 | 4 | 4 | 8 |
| 1.322 | 1.310 | 1.318 | 1.237 | 1.283 | 1.426 | 1.194 |
| 0.100 | 0.105 | 0.096 | 0.085 | 0.099 | 0.113 | 0.081 |
| 1.90—23.25 | 2.29—23.24 | 2.37—23.33 | 1.75—23.40 | 1.73—23.30 | 2.10—23.29 | 1.67—23.30 |
| 6113 | 6121 | 8157 | 4743 | 8119 | 9991 | 17633 |
| 2129 | 2071 | 2750 | 1628 | 2746 | 1975 | 3605 |
| 0.1466 | 0.0638 | 0.0961 | 0.0721 | 0.0364 | 0.0656 | 0.1510 |
| 1142 | 1708 | 1273 | 990 | 2346 | 2756 | 2756 |
| 252 | 250 | 349 | 197 | 340 | 255 | 314 |
| 0.0740 | 0.0401 | 0.0553 | 0.0465 | 0.0395 | 0.0373 | 0.1313 |
| 0.1842 | 0.0993 | 0.1087 | 0.0799 | 0.0889 | 0.1001 | 0.3721 |
| 0.1361 | 0.0484 | 0.1361 | 0.0857 | 0.0509 | 0.0460 | 0.1485 |
| 0.2373 | 0.1042 | 0.1382 | 0.0923 | 0.0945 | 0.1068 | 0.3839 |
| 0.732 | 0.953 | 0.757 | 0.840 | 1.014 | 0.753 | 2.556 |

[**3e**′ + $H^+$]$^-$ (62), 251 (100), 233 (23). Found (%): C, 32.7; H, 4.0; N, 11.9; Pb, 23.8. $C_{22}H_{26}K_2N_8O_8Pb \cdot 3MeOH$. Calculated (%): C, 32.9; H, 4.2; N, 12.3; Pb, 22.7.

**Monopotassium 3-(4,4,5,5-tetramethyl-3-oxido-1-oxyl-4,5-dihydro-1*H*-imidazol-2-yl)-1*H*-pyrazole-4,5-dicarboxylate (K3d″).** A 10% aqueous KOH solution (20 mL) was added to a stirred suspension of **13c** (3.43 g, 18.6 mmol) and **2** (2.76 g, 18.6 mmol) in MeOH (60 mL). The resulting solution was stirred for 4 h, during which a white precipitate gradually formed. The precipitate was filtered off, dissolved in water (10 mL), and oxidized with $PbO_2$ (15.0 g, 62.7 mmol). The solvent was distilled off, and the residue was washed with acetone, filtered off, and recrystallized from an EtOH—toluene mixture. The yield was 2.49 g, a dark-violet powder. IR, ν/cm$^{-1}$: 801, 837, 854, 874, 1117, 1171, 1221, 1289, 1355, 1400, 1429, 1458, 1505, 1581, 2986, 3174, 3448, 3584. Found (%): C, 31.9; H, 3.1; N, 11.3. According to the results of chelate titration, the sample contained no Pb. MS, *m/z* ($I_{rel}$ (%)): 311 [**3d**′ + 2$H^+$ + 1]$^-$ (15.0), 310 [**3d**′ + 2$H^+$]$^-$ (100), 294 (31), 266 (60), 250 (20). The most probable composition of $K_3$**3d**′$\cdot 2H_2O$ was $C_{12}H_{12}K_3N_4O_6 \cdot 2H_2O$. Calculated (%): C, 31.2; H, 3.5; N, 12.1.

A solution of $H_2SO_4$ (0.67 g, 6.8 mmol) in EtOH (10 mL) was added dropwise to a solution of the product (1.42 g, 3.1 mmol with respect to $K_3$**3d**′$\cdot 2H_2O$) in EtOH (20 mL). The precipitate was filtered off, sodium formate (0.48 g) was added to the filtrate, and the filtrate was concentrated. Ethanol (~50 mL) was added to the residue, the insoluble precipitate was filtered off, and the filtrate was concentrated. The residue was dissolved in a minimum amount of EtOH (~15 mL) with slight heating (~40 °C) and kept at 0 °C for one week. The precipitate that formed was composed of pale-brown crystals and a yellow powder. The precipitate was filtered off, washed with diethyl ether, and dried in air. X-ray diffraction study of the crystals demonstrated that they consist of the ions of compound **15**. The filtrate was concentrated. The residue was dissolved in a minimum amount of water (~5 mL) with slight heating (~40 °C) and kept at 0 °C for three days. The red-violet powdered precipitate that formed was filtered off and washed with acetone. The yield was 150 mg (13%); $\mu_{eff}$ = 1.72 $\mu_B$ (300 K). IR, ν/cm$^{-1}$: 781, 798, 874, 1003, 1127, 1177, 1250, 1329, 1368, 1418, 1481, 1529, 1575, 1613, 2852, 2922, 2992, 3251. MS, *m/z* ($I_{rel}$ (%)): 312 [**3d″** + 2] (2.3), 311 [**3d″** + 1]$^-$ (15.2), 310 [**3d″**]$^-$ (100), 266 (86), 222 (18). Found (%): C, 40.8; H, 4.1; N, 15.9. $C_{12}H_{14}N_4O_6K$. Calculated (%): C, 41.3; H, 4.0; N, 16.0. The successive reactions of K**3d″** with NaH and EtI in DMF afforded **3b** (TLC data). The reaction of K**3d″** with an equivalent amount of $H_2SO_4$ in EtOH yielded a diamagnetic yellow-brown product.

**3-(4,4,5,5-Tetramethyl-3-oxido-1-oxyl-4,5-dihydro-1*H*-imidazol-2-yl)-1*H*-pyrazole-5-carboxylic acid (3e)** was synthesized analogously to K**3d″** from Pb(K**3e**′)$_2$ (0.24 g, 0.26 mmol). The crude product was recrystallized from a $CH_2Cl_2$—toluene mixture. The yield was 60 mg (43%), dark-blue needle-like crystals; $\mu_{eff}$ = 1.73 $\mu_B$ (300 K). IR, ν/cm$^{-1}$: 770, 789, 848, 997, 1019, 1091, 1138, 1174, 1227, 1284, 1374, 1400, 1472, 1639, 1722, 2992, 3275, 3390. Found (%): C, 47.2; H, 5.9; N, 18.7. $C_{11}H_{15}N_4O_4 \cdot H_2O$. Calculated (%): C, 46.3; H, 6.0; N, 19.6. The successive reactions of **3e** with NaH and EtI in DMF produced **3c** (TLC data).

**Bis[3,5-(4,4,5,5-tetramethyl-3-oxido-1-oxyl-4,5-dihydro-1*H*-imidazol-2-yl)]-1*H*-pyrazole (4).** The compound **2**$\cdot H_2SO_4 \cdot H_2O$ (0.9 g, 3.4 mmol) was added to a stirred suspension of **12a** (0.29 g, 1.7 mmol) in water (4.5 mL). The reaction mixture was stirred for two days. The resulting pale-yellow solution was transferred into a beaker, $CHCl_3$ (12 mL) was added, the reaction mixture was carefully neutralized with $NaHCO_3$ until elimination of $CO_2$ ceased, and $NaIO_4$ (0.58 g, 2.7 mmol) was added portionwise for 1 h. The reaction mixture was stirred for 20 min, the organic phase was separated, and the aqueous phase was extracted with $CHCl_3$ (1×20 mL). The combined organic solutions were dried with $Na_2SO_4$ and filtered. Heptane (20 mL) was added to the filtrate, and the solution was concentrated to 20 mL. The dark-blue crystals that formed were filtered off. The yield was 0.3 g (47%). The compound decomposes at 195—210 °C; $\mu_{eff}$ = 2.42 $\mu_B$ (300 K). IR, ν/cm$^{-1}$: 844, 866, 988, 1024, 1082, 1139, 1162, 1211, 1344, 1373, 1421, 1451, 2988, 3267. High-resolution MS. Found: *m/z* 378.2009 $[M]^+$. $C_{17}H_{26}N_6O_4$. Calculated: M = 378.2015. MS, *m/z* ($I_{rel}$ (%)): 378 (2), 249 (14), 248 (19), 84 (100), 69 (41), 56 (18). Found (%): C, 52.6; H, 7.3; N, 21.7. $C_{17}H_{26}N_6O_4 \cdot 0.5H_2O$. Calculated (%): C, 52.7; H, 7.0; N, 21.7.

The reaction of **12a** and $NaIO_4$ in a molar ratio of 1 : 2 afforded a blue-green product, which was suspended in ethyl acetate (~20 mL). The poorly soluble by-product was filtered off. The filtrate was concentrated and recrystallized from a $CH_2Cl_2$—heptane mixture. The yield of **4** was 0.3 g (17%). The weight of the by-product was 0.56 g. Crystallization of the by-product from a mixture of $CH_2Cl_2$ and toluene afforded crystals of 5-(4,4,5,5-tetramethyl-3-oxido-4,5-dihydro-1*H*-imidazol-2-yl)-3-(4,4,5,5-tetramethyl-3-oxido-1-oxyl-4,5-dihydro-1*H*-imidazol-2-yl)-1*H*-pyrazole (**16**).

**X-ray diffraction study.** X-ray diffraction data sets for all compounds were collected on a Smart Apex diffractometer (λMo-Kα, graphite monochromator). The structures were solved by direct methods and refined by the full-matrix least-squares method using the SHELXTL program package. The positions of a number of H atoms were located from difference electron density maps. The positions of the other H atoms were calculated geometrically and refined using a riding model (a rigid-body approximation).

Crystals suitable for X-ray diffraction study were grown by crystallization of the compounds from the following solvents and their mixtures (v/v): **1a**, acetone—heptane; **1c**, $C_6H_6$—heptane (1 : 1); **1d**, diethyl ether—heptane; **3a**, toluene; **3c**, $CH_2Cl_2$—heptane (1 : 1); **3e**$\cdot H_2O$, MeOH—$H_2O$; **4**, $CH_2Cl_2$—heptane; and **10**, toluene—heptane (1 : 2).

Principal crystallographic characteristics and details of X-ray diffraction studies are given in Table 1.

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## References


1. V. I. Ovcharenko, K. Yu. Maryunina, S. V. Fokin, E. V. Tretyakov, G. V. Romanenko, and V. N. Ikorskii, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 2304 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 2406].
2. P. Rey and V. I. Ovcharenko, in *Magnetism: Molecules to Materials IV,* Eds J. S. Miller and M. Drillon, Wiley-VCH, Weinheim, 2003, vol. **4**.
3. S. Yamada, T. Ishida, and T. Nogami, *J. Chem. Soc., Dalton Trans.*, 2004, 898.
4. S. F. Vasilevsky, E. V. Tretyakov, V. N. Ikorskii, G. V. Romanenko, S. V. Fokin, Y. G. Shwedenkov, and V. I. Ovcharenko, *Arkivoc*, 2001, **ix**, 55.
5. V. I. Ovcharenko, S.V. Fokin, G.V. Romanenko, Yu. G. Shvedenkov, V.N. Ikorskii, E. V. Tretyakov, and S. F. Vasilevskii, *Zh. Strukt. Khim.,* 2002, **43**, 163 [*J. Struct. Chem.*, 2002, **43** (Engl. Transl.)].
6. L. Catala, R. Feher, D. B. Amabilino, K. Wurst, and J. Veciana, *Polyhedron*, 2001, **20**, 1563.
7. C. V. Greco and F. Pellegrini, *J. Chem. Soc., Perkin Trans. 1*, 1972, 720.
8. K. von Auwers and O. Ungemach, *Ber. Deutsch. Chem. Ges.*, 1933, **66**, 1205.
9. Hüttel, *Ber. Dtsch. Chem. Ges.*, 1941, **74**, 1680.
10. F. A. Carey and R. J. Sundberg, *Adv. Org. Chem.*, **2**, Plenum Press, New York, London, 1977, Part 6.1.2.
11. *Science of Synthesis: Houben-Weyl Methods of Molecular Transformations,* Category 2, **12**, Ed. R. Neyer, Georg Thieme Verlag, Stutgart—New York, 2002, Part 12.1.1.3.1.1.1.
12. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
13. L. B. Volodarsky, V. A. Reznikov, and V. I. Ovcharenko, *Synthetic Chemistry of Stable Nitroxides*, CRC Press, Florida, 1994.
14. K. E. Nosova, E. V. Tretyakov, G. V. Romanenko, and V. I. Ovcharenko, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 2113 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 2231].
15. V. I. Ovcharenko, S. V. Fokin, and P. Rey, *Mol. Cryst. Liq. Cryst.*, 1999, **334**, 109.
16. V. I. Ovcharenko, S. V. Fokin, G. V. Romanenko, I. V. Korobkov, and P. Rey, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1539 [*Russ. Chem. Bull.*, 1999, **48**, 1519 (Engl. Transl.)].
17. *Org. Syntheses Coll.*, 1988, **6**, 954.
18. *Org. Syntheses Coll.*, 1943, **2**, 165.
19. S. S. Gitis, A. I. Glaz, and A. V. Ivanov, *Praktikum po organicheskoi khimii. Organicheskii sintez* [*Laboratory Manual on Organic Chemistry. Organic Synthesis*], Vysshaya shkola, Moscow, 1991 (in Russian).
20. R. Přibil, *Komplexony v chemické analyse*, Nakladatelství Československé akademie věd, Praha, 1957.
21. R. Duschinsky and L. A. Dolan, *J. Am. Chem. Soc.*, 1946, **68**, 2350.
22. W. Kirmse and M. Buschhoff, *Chem. Ber.*, 1967, **100**, 1491.
23. H. Abdallah and R. Grée, *Tetrahedron Lett.*, 1980, **21**, 2239.


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