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A novel route to spin-labeled dihydrooxepines and *o*-benzoquinones*

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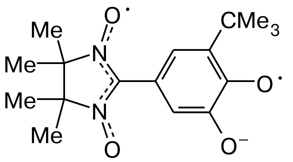
A reaction of a lithiated derivative of 4,4,5,5-tetramethyl-3-oxido-4,5-dihydro-1*H*-imidazole 1-oxyl with 3,6-di-*tert*-butyl-*o*-benzoquinone at –80 °C predominantly gave spin-labeled dihydrooxepine *via* nucleophilic 1,2-addition of the paramagnetic carbanion to the CO group of the benzoquinone followed by insertion of the O atom into the ring. At lower temperatures, this reaction was accompanied by 1,4-addition of the organolithium compound to the benzoquinone followed by oxidation of the resulting adduct into spin-labeled *o*-benzoquinone. This "one pot" process is a novel approach to organic derivatives that can further be converted into di- and polyradicals combining nitronyl nitroxide and semiquinolate fragments.

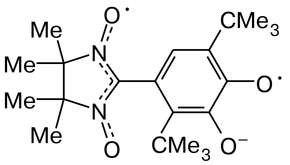
Key words: nitronyl nitroxides, *o*-benzoquinones, ring expansion reactions, $S_N{}^H$-reactions.

Design of molecular magnets based on heterospin complexes of transition metals with organic radicals is an actively developed interdisciplinary scientific field. One of these goals is the design of novel types of magnetically active compounds liable to either a phase transition into a magnetically ordered state or structural rearrangements giving rise to a physical anomaly in the paramagnetic range.[1—3] The ability of heterospin complexes to demonstrate various magnetic anomalies is due to the presence of exchange-coupled spin systems (also called exchange clusters, multispin ensembles, or multispin clusters).[4,5] The largest groups of paramagnetic ligands used to design such clusters are constituted by stable nitroxides, in which the unpaired electron density is efficiently delocalized over several donor atoms,[2,6] and sterically hindered *o*-semiquinolate anions.[7,8] In a considerable number of complexes with such ligands, the solid phases can be magnetized and exhibit thermomagnetic or photo/thermomechanical properties.[9—11]

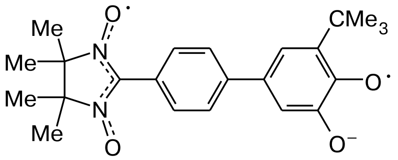
Simultaneous introduction of various paramagnetic fragments (nitroxide and *o*-semiquinolate groups) into the ligand environment of a metal ion gives greater scope to the design and functionalization of multispin ensembles. For instance, heterospin Cu^{II} and Co^{II} complexes with various paramagnetic ligands (an *o*-semiquinolate radical anion and stable nitroxides derived from 2-imidazoline) have been recently[12,13] obtained and characterized. They exhibit nontrivial properties. For instance, when coordinating to an extra ligand, Cu^{II} semiquinolate begins to function as a sensor of its nearest environment, using the changes in the ferromagnetic/antiferromagnetic exchange ratio as a quantum inducing device.[12] Heterospin cobalt complexes containing both the *o*-semiquinolate and nitroxide ligands show magnetic anomalies at room temperature, which is promising for the design of new inducing devices and molecular actuators.[13] Active investigations[14—16] are being done to obtain complexes with diradical anions L^n in which the *o*-semiquinone ring is linked directly or



L^1



L^3



L^2

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through the *para*-phenylene spacer with the 3-oxido-1-oxylimidazolin-2-yl fragment. Precursors of L^n are spin-labeled catechols prepared by condensation of appropriate aldehydes with 2,3-bis(hydroxyamino)-2,3-dimethylbutane followed by oxidation of intermediate imidazolidine-1,3-diols. The methodological basis for the synthesis of such ligands L^n is provided by Ullman´s approach.[17,18]

In the present work, we propose a novel method for the synthesis of such organic paramagnetics. The method involves nucleophilic addition reactions of organometallic compounds of Li, Zn, Cd, and Al (Scheme 1) with sterically shielded 3,6-di-*tert*-butyl-*o*-benzoquinone (**2**). Subsequent hydrolysis and oxidation give the corresponding substituted *o*-quinones.[19] If the reaction followed the 1,4-addition pattern, the reaction product could *a priori* be expected to be 2-(2,5-di-*tert*-butyl-3,4-dioxocyclohexa-1,5-dienyl)-4,4,5,5-tetramethyl-3-oxido-4,5-dihydro-1*H*-imidazole 1-oxyl (**5**) (see Scheme 1), which is a potential precursor of the diradical anion L^3. This was evidenced by a 1,4-addition reaction of benzoquinone **2** with PhLi at one carbonyl group: the resulting lithium semiquinolate was subjected to *in situ* hydrolysis and oxidation leading to phenyl-*o*-benzoquinone.[20] At the same time, it is known[21] that the first step in reactions of benzoquinone **2** with lithium acetylenides (PhC≡CLi or $Me_3CC≡CLi$) involves 1,2-addition of the organolithium compound to the *o*-quinone to yield the corresponding lithium salts of hydroxycyclohexadienones, which in polar solvents undergo rearrangement into seven-membered lactones. Thus, the problem of introduction of a paramagnetic substituent into quinone **2** *via* its reaction with compound **1** remained unsolved up to the present study.

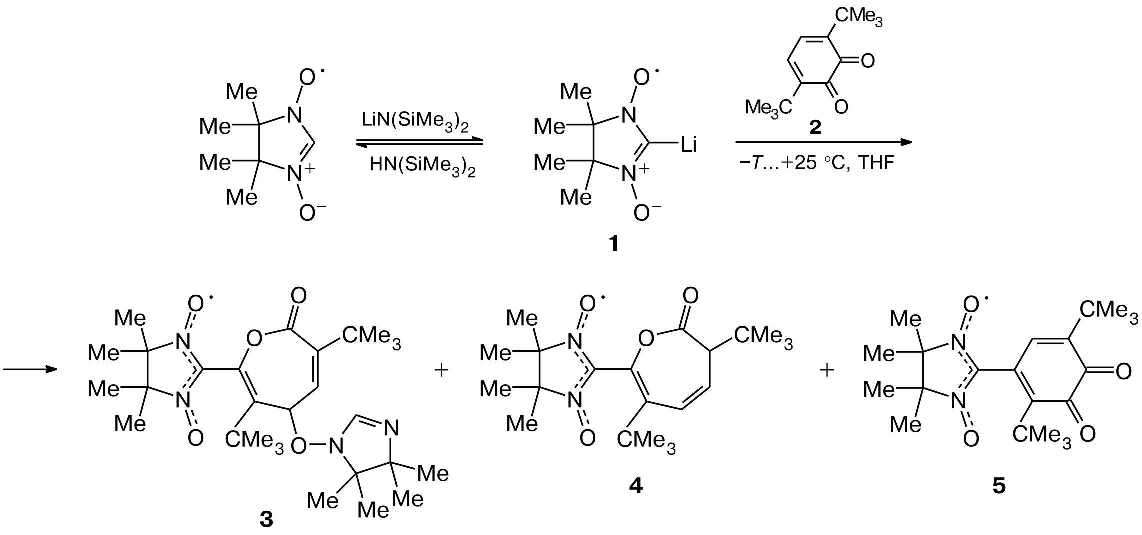
We found that a reaction of lithiated derivative **1** (generated by the action of $LiN(SiMe_3)_2$ on 4,4,5,5-tetramethyl-3-oxido-4,5-dihydro-1*H*-imidazole 1-oxyl) with *o*-quinone **2** in THF gives a mixture of products varying with the reaction temperature and time (see Scheme 1). For instance, when compounds **1** and **2** were stirred at −80 °C for 2 h, the final mixture contained dihydrooxepine **4** (23%) and its transformation product **3** (26%). When the reagents were mixed at −80 °C, warmed to room temperature, and stirred for 24 h, we detected no dihydrooxepine **4**, while the yield of compound **3** increased to 47%. When the reaction was carried out at −105 °C (the gel transition temperature of THF) for 2 h, workup of the reaction mixture mainly gave nitroxides **3** and **4**; minor amounts of quinone **5** were also isolated. When the stirring time was extended to 24 h, dihydrooxepine **4** was transformed into compound **3** (42%), while the yield of quinone **5** did not exceed 5%.

Therefore, lithiated derivative **1** reacts with the starting *o*-quinone **2** predominantly according to the 1,2-addition mechanism to give adduct **6**, which undergoes *in situ* rearrangement into lactone **7** (Scheme 2).

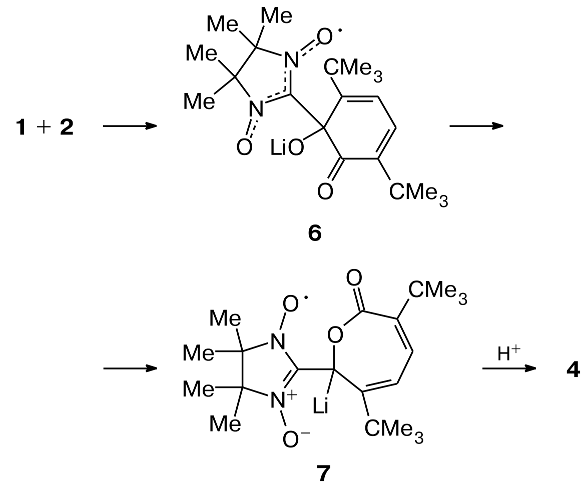
One can believe that warming of the reaction mixture results in a further transformation of lactone **7**: the Li atom migrates to the nitronyl O atom to give isomer **8**, which then recombines with imino nitroxide **9** gradually accumulating in the reaction mixture through deoxygenation of the starting 4,4,5,5-tetramethyl-3-oxido-4,5-dihydro-1*H*-imidazole 1-oxyl (Scheme 3).

Single crystals of nitroxides **3**—**5** were grown and examined by X-ray diffraction. In structures **3** and **4**, the dihydrooxepine ring has a boat conformation. The C(8), C(9), C(22), and C(23) atoms in compound **3** (pairs of the doubly bonded atoms: C(8)=C(9), 1.330(3) Å; C(22)=C(23), 1.331(3) Å) and the C(14), C(22), C(28), and O(5) atoms in compound **4** form the bottom of the boat; the devia-

Scheme 1



Scheme 2



tions of the aforementioned atoms from the mean-square plane do not exceed 0.025 Å (Fig. 1, Table 1). The other atoms of the dihydrooxepine ring are distant from the bottom plane by 0.71—0.77 and 0.75—0.83 Å in compounds **3** and **4**, respectively. The angles between the planes of the fragment N(1)C(7)N(2) of the imidazoline ring and the fragment O(5)C(8)C(9) of the dihydrooxepine ring are 81.5° and 76.6° in compounds **3** and **4**, respectively. The N—O bond lengths in nitroxides **3** and **4** are 1.277(2)—1.280(2) Å, which is characteristic of nitronyl nitroxides.[22] The paramagnetic centers of adjacent molecules (the O atoms of the N—O groups) are spaced apart at more than 4.5 Å. The considerable intermolecular distances make the spins virtually separate, so the experimental effective magnetic moments μ_{eff} of compounds **3** and **4** in a temperature range from 300 to 30 K are constant and close to a theoretical value of $1.73\mu_B$.

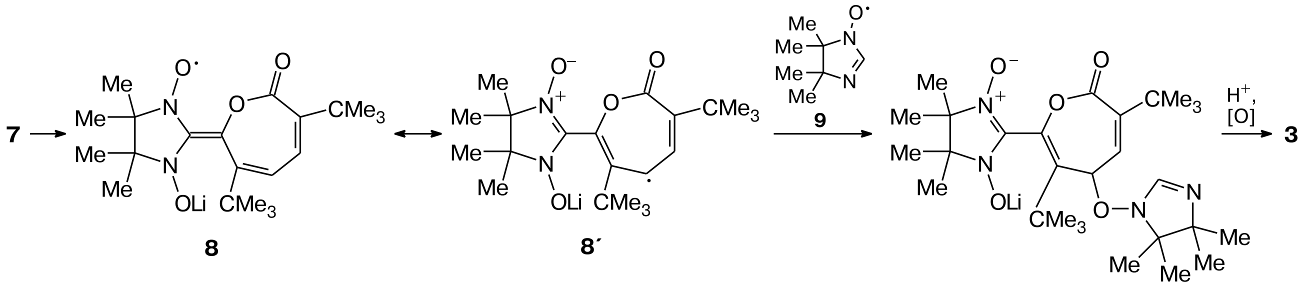
The structure of nitroxide **5** has a plane of mirror symmetry passing through the C and O atoms of the quinone fragment and the C(10), C(11), C(24), and C(27) atoms of the *tert*-butyl groups (Fig. 2, *a*). The planar imidazoline ring is perpendicular to the plane of the benzene ring. The N—O bond lengths in the nitronyl nitroxide fragment are equal (1.277(2) Å). The intermolecular contacts O(1)...C(14´) (2.888(2) Å) between the molecules of compound **5** are substantially shorter than the sum of the van der Waals radii (–0.332 Å) (Fig. 2, *b*). Apparently, the presence of such contacts accounts for the difference between the geometrical parameters of two molecular fragments (O=)C—CBu^t. In the fragment (O=)C—CBu^t with the carbonyl C atom approaching the O atoms of the N—O groups of adjacent molecules, the C(9)—C(14) and C(14)—O(3) bond lengths are 1.498(3) and 1.215(3) Å, respectively. The corresponding bond lengths in the other fragment are different: C(22)—C(23), 1.467(3) Å; C(22)—O(4), 1.225(3) Å. The μ_{eff} value of compound **5** in a temperature range from 40 to 300 K is close to the theoretical value for a monoradical ($1.73\pm0.01\mu_B$).

The ESR spectra of compounds **3**—**5** are similar, consisting of a quintet for two virtually equivalent N nuclei. The spectra show no finer substructure, which is probably due to the steric hindrances presented by the bulky substituents to the rotation of the radicals in solution (in Fig. 3, the ESR spectrum of nitroxide **5** is shown as an example). Nevertheless, for satisfactory modeling of the spectral lines, we should take account of the HFC with 12 methyl protons with a characteristic constant of 0.024 mT. The calculated HFC constants and *g* factors are given below (the accuracy of the calculation is 0.005 mT and 0.0001, respectively).

Compound	a_{N1}	a_{N2}	a_{12H}	g_{iso}
	mT			
3	0.736	0.712	0.024	2.0066
4	0.747	0.712	0.024	2.0065
5	0.728	0.717	0.024	2.0066

To sum up, we found that a reaction of 3,6-di-*tert*-butyl-*o*-benzoquinone with a lithium derivative of 4,4,5,5-tetramethyl-3-oxido-4,5-dihydro-1*H*-imidazole 1-oxyl occurs at the carbonyl group of the quinone according to the 1,2-addition pattern followed by insertion of the O atom into the ring. The resulting substituted dihydrooxepine **4** can react with lithium 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-olate to give more substituted di-

Scheme 3



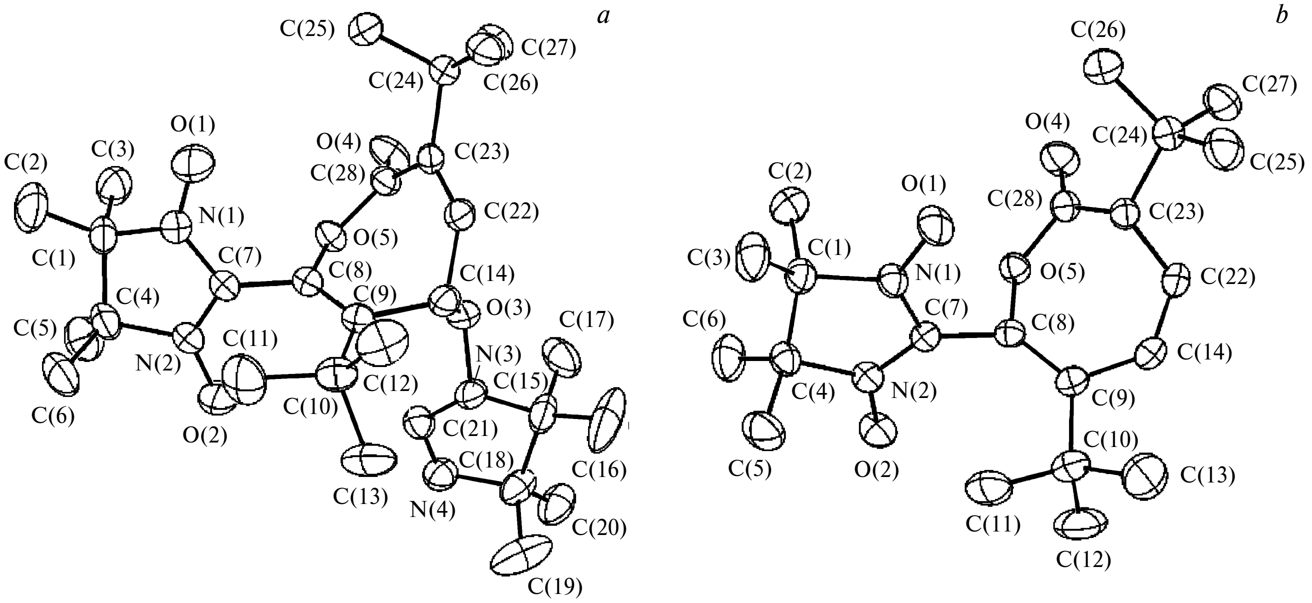


Fig. 1. Structures **3** (*a*) and **4** (*b*).

Table 1. Selected bond lengths *d* in structures **3** and **4**

Bond	*d*/Å		Bond	*d*/Å	
	3	**4**		**3**	**4**
N(1)—O(1)	1.280(2)	1.280(2)	C(22)—C(23)	1.331(3)	1.500(3)
N(2)—O(2)	1.279(2)	1.277(2)	C(23)—C(28)	1.484(3)	1.505(3)
O(4)—C(28)	1.196(2)	1.193(2)	O(3)—N(3)	1.427(2)	—
O(5)—C(28)	1.386(2)	1.395(2)	O(3)—C(14)	1.447(2)	—
O(5)—C(8)	1.406(2)	1.411(2)	N(3)—C(21)	1.390(3)	—
C(7)—C(8)	1.463(3)	1.473(3)	N(3)—C(15)	1.490(3)	—
C(8)—C(9)	1.330(3)	1.333(3)	N(4)—C(21)	1.266(3)	—
C(9)—C(14)	1.525(3)	1.473(3)	N(4)—C(18)	1.487(3)	—
C(14)—C(22)	1.497(3)	1.317(3)			

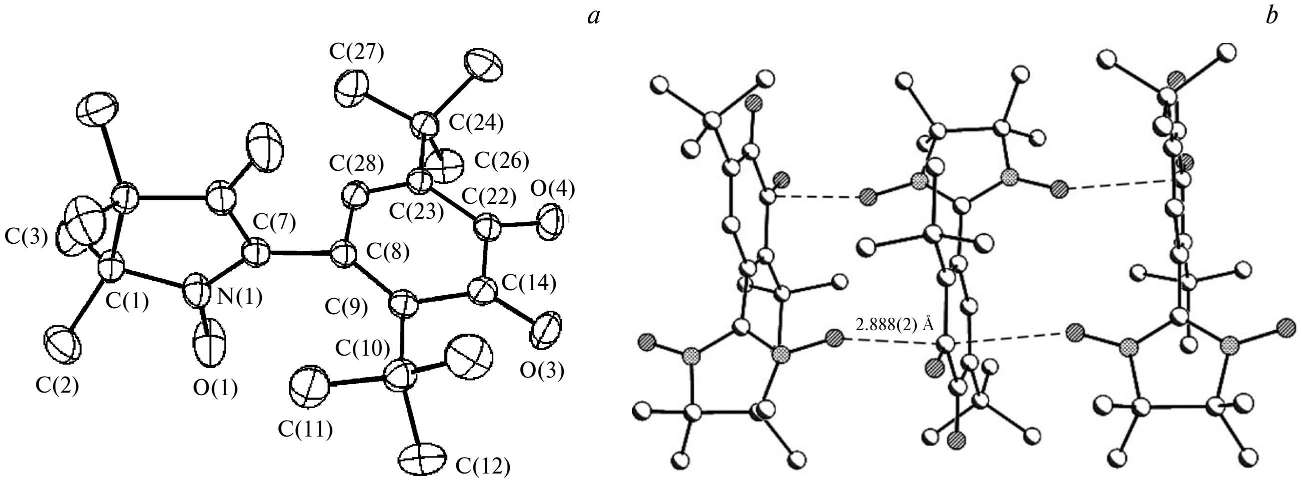


Fig. 2. Structure **5** (*a*) and the intermolecular contacts O(1)...C(14′) in structure **5** (*b*). The symmetry operation code is 1 – *x*, –1/2 + *y*, 1 – *z*.

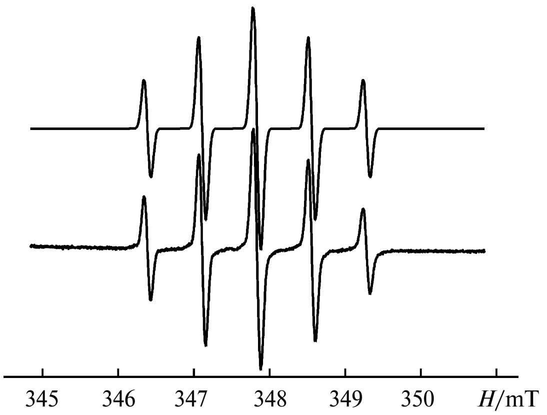


Fig. 3. ESR spectrum of a $1 \cdot 10^{-5}$ *M* solution of nitroxide **5** in toluene.

hydrooxepine **3**. At low temperatures (–105 °C), the above process is accompanied by 1,4-addition of the organolithium compound leading to spin-labeled quinone **5**, which is formally derived from compound **2** by an $S_N{}^H$-reaction at the quinonoid ring.

As noted above, L^1 and L^2 were earlier accessible from appropriate catechols,[14—16] which were oxidized into diradical anions for complexation reactions with metal ions. The method we proposed here for the synthesis of spin-labeled derivatives affords quinone **5**, which can be reduced to diradical anion L^3 and, like L^1 and L^2, used in complexation reactions. The latter calls for further investigations.

Experimental

4,4,5,5-Tetramethyl-3-oxido-4,5-dihydro-1*H*-imidazole 1-oxyl (**1**)[23] and 3,6-di-*tert*-butyl-*o*-benzoquinone (**2**)[24] were prepared according to known procedures. Commercial reagents and solvents were used as purchased. Reactions were carried out under argon. Silica gel (0.063—0.200 mm, column chromatography grade, Merck) and Al_2O_3 (chromatography grade, the Donetsk Plant of Chemicals) were used for chromatographic purposes. IR spectra (KBr pellets) were recorded on a Vector-22 spectrophotometer (Bruker). Melting points were measured on a Boetius microscope stage. Microanalyses were performed at the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry (Siberian Branch of the Russian Academy of Sciences) on a Euro EA3000 CHNS-analyzer. Magnetochemical measurements were carried out on a MPMSXL SQUID magnetometer (Quantum Design) in the 2—300 K range. The effective magnetic moments were calculated by the equation

$$\mu_{\text{eff}}(T) = 2.84(\chi'_M T)^{1/2},$$

where χ'_M is the paramagnetic molar susceptibility corrected to the diamagnetic contribution. The steady-state X-band ESR spectra of $1 \cdot 10^{-5}$ *M* solutions of nitroxyl radicals in toluene were recorded at room temperature on a Bruker EMX spectrometer and modeled with the Winsim v.0.96 program package;[25] the isotropic *g* factors were determined with solid-state diphenylpicrylhydrazyl as a standard.

Reaction of a lithiated derivative of 4,4,5,5-tetramethyl-3-oxido-4,5-dihydro-1*H*-imidazole 1-oxyl (1) with 3,6-di-*tert*-butyl-*o*-benzoquinone (2) (general procedure *A*). A 1.0 *M* solution of $LiN(SiMe_3)_2$ (2.1 mL, 2.1 mmol) in THF was added at –80 °C to a stirred solution of 4,4,5,5-tetramethyl-3-oxido-4,5-dihydro-1*H*-imidazole 1-oxyl (300 mg, 1.91 mmol) in THF (40 mL). The resulting red-orange solution was stirred for 30 min and cooled until a jelly-like mass formed (~–105 °C). Then a solution of benzoquinone **2** (300 mg, 1.36 mmol) in THF (5 mL) was added. The reaction mixture was stirred without cooling for 20 h and concentrated. The residue was chromatographed on SiO_2 (2×10 cm) with CH_2Cl_2 and AcOEt as eluents used in succession. The yield of nitroxide **3** was 294 mg (42% from quinone **2**). A mixture of compounds **5** and **2** was separated by column chromatography on Al_2O_3 (2×10 cm) with benzene and AcOEt as eluents used in succession. The yield of nitroxide **5** was 23 mg (5%).

General procedure *B*. A 1.0 *M* solution of $LiN(SiMe_3)_2$ (2.1 mL, 2.1 mmol) in THF was added at –80 °C to a stirred solution of 4,4,5,5-tetramethyl-3-oxido-4,5-dihydro-1*H*-imidazole 1-oxyl (1.91 mmol) and compound **2** (1.36 mmol) in THF (40 mL). The reaction mixture was stirred without cooling for an additional 2 h and concentrated. The residue was chromatographed on SiO_2 (2×10 cm) with CH_2Cl_2 and AcOEt as eluents used in succession. The yield of nitroxide **3** was 186 mg (26% from quinone **2**). A mixture of compounds **4** and **2** was separated by column chromatography on Al_2O_3 (2×10 cm) with benzene and AcOEt as eluents used in succession. The yield of nitroxide **4** was 120 mg (23%).

2-[3,6-Di-*tert*-butyl-2-oxo-5-(4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-yloxy)-2,5-dihydrooxepin-7-yl]-4,4,5,5-tetramethyl-3-oxido-4,5-dihydro-1*H*-imidazole 1-oxyl (3). Violet needles, m.p. 147—149 °C (from ethyl acetate—toluene), R_f 0.40 (CH_2Cl_2, N/UV$_{254}$ Al_2O_3 plates (0.2 mm, Macherey-Nagel)); R_f 0.33 (AcOEt, Silica gel 60 F$_{254}$ plates (Merck)). IR, ν/cm^{-1}: 544, 610, 647, 678, 700, 737, 752, 824, 842, 870, 920, 941, 962, 983, 1024, 1046, 1072, 1094, 1121, 1164, 1217, 1249, 1337, 1371, 1410, 1464, 1611, 1735, 2873 (w), 2982. $\mu_{\text{eff}} = 1.73\mu_B$ (200—300 K). Found (%): C, 64.8; H, 8.6; N, 10.7. $C_{28}H_{45}N_4O_5$. Calculated (%): C, 65.0; H, 8.8; N, 10.8.

2-(3,6-Di-*tert*-butyl-2-oxo-2,3-dihydrooxepin-7-yl)-4,4,5,5-tetramethyl-3-oxido-4,5-dihydro-1*H*-imidazole 1-oxyl (4). Violet crystals, m.p. 158—159 °C (from CH_2Cl_2—heptane), R_f 0.62 (CH_2Cl_2, Al_2O_3); R_f 0.77 (AcOEt, silica gel). IR, ν/cm^{-1}: 543, 617, 650, 667, 688, 731, 755, 777, 837, 871, 885, 932, 949, 965, 978, 1003, 1030, 1060, 1077, 1089, 1137, 1172, 1218, 1257, 1338, 1371, 1408, 1454, 1592, 1785, 2872 (w), 2968, 2999, 3056 (w), 3400 (br). $\mu_{\text{eff}} = 1.73\mu_B$ (250—300 K). Found (%): C, 66.3; H, 8.8; N, 7.4. $C_{21}H_{33}N_2O_4$. Calculated (%): C, 66.8; H, 8.8; N, 7.4.

2-(2,5-Di-*tert*-butyl-3,4-dioxocyclohexa-1,5-dienyl)-4,4,5,5-tetramethyl-3-oxido-4,5-dihydro-1*H*-imidazole 1-oxyl (5). Red-brown needles, m.p. 204—206 °C (from CH_2Cl_2—heptane), R_f 0.73 (CH_2Cl_2, Al_2O_3); R_f 0.74 (AcOEt, silica gel). IR, ν/cm^{-1}: 551, 644, 673, 734, 870, 939, 1142, 1173, 1216, 1273, 1370, 1398, 1451, 1488, 1657, 1673, 1688, 2920 (w), 2958, 2993. $\mu_{\text{eff}} = 1.68\mu_B$ (250—300 K). Found (%): C, 67.0; H, 8.1; N, 7.5. $C_{21}H_{31}N_2O_4$. Calculated (%): C, 67.2; H, 8.3; N, 7.5.

X-ray diffraction study of compounds 3—5. Reflection intensities were collected on a SMART APEX II CCD diffractometer (Bruker AXS) (Mo-Kα radiation, λ = 0.71073 Å, *T* = 240 K).

Absorption corrections were applied with the SADABS program (v. 2.10, Bruker). The structures were solved by direct methods and refined anisotropically (for all non-hydrogen atoms) by the full-matrix least-squares method. The H atoms were partially located from difference electron-density maps. All calculations were performed with the Bruker SHELXTL program package (version 6.14).

Compound **3**. $C_{28}H_{45}N_4O_5$, M = 517.68, monoclinic crystals, space group $P2_1/c$, a = 19.461(7) Å, b = 11.770(4) Å, c = 13.410(5) Å, β = 96.928(8)°, V = 3049.3(18) Å^3, Z = 8, d_{calc} = 1.128 g cm^{-3}, μ = 0.078 mm^{-1}, 23 736 measured reflections (2.03° < θ < 27.95°), 7211 independent reflections, 2965 reflections with $I > 2\sigma(I)$, 347 parameters refined, R_1 = 0.0532, wR_2 = 0.1302.

Compound **4**. $C_{21}H_{33}N_2O_4$, M = 377.49, orthorhombic crystals, space group $Pbca$, a = 10.3434(13) Å, b = 12.3847(16) Å, c = 34.433(5) Å, V = 4410.8(10) Å^3, Z = 8, d_{calc} = 1.137 g cm^{-3}, μ = 0.078 mm^{-1}, 35 427 measured reflections (2.37° < θ < 28.04°), 5271 independent reflections, 1890 reflections with $I > 2\sigma(I)$, 377 parameters refined, R_1 = 0.0439, wR_2 = 0.1001.

Compound **5**. $C_{21}H_{31}N_2O_4$, M = 375.48, monoclinic crystals, space group $P2/m$, a = 9.5529(16) Å, b = 10.1119(18) Å, c = 11.436(2) Å, β = 112.490(12)°, V = 1020.7(3) Å^3, Z = 8, d_{calc} = 1.222 g cm^{-3}, μ = 0.084 mm^{-1}, 14 913 measured reflections (2.31° < θ < 28.44°), 2680 independent reflections, 993 reflections with $I > 2\sigma(I)$, 208 parameters refined, R_1 = 0.0438, wR_2 = 0.1044.

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