Reactions of cyclic α-methoxy nitrones with nucleophilic reagents

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Reactions of cyclic α-methoxy nitrones, which are derivatives of imidazole or dihydroimidazole *N*-oxides, with amines, KOH, or KSH result in the replacement of the MeO group to form cyclic α-amino nitrones, hydroxamic acids, or thiohydroxamic acids, respectively. Analogous reactions occur with C-nucleophiles.

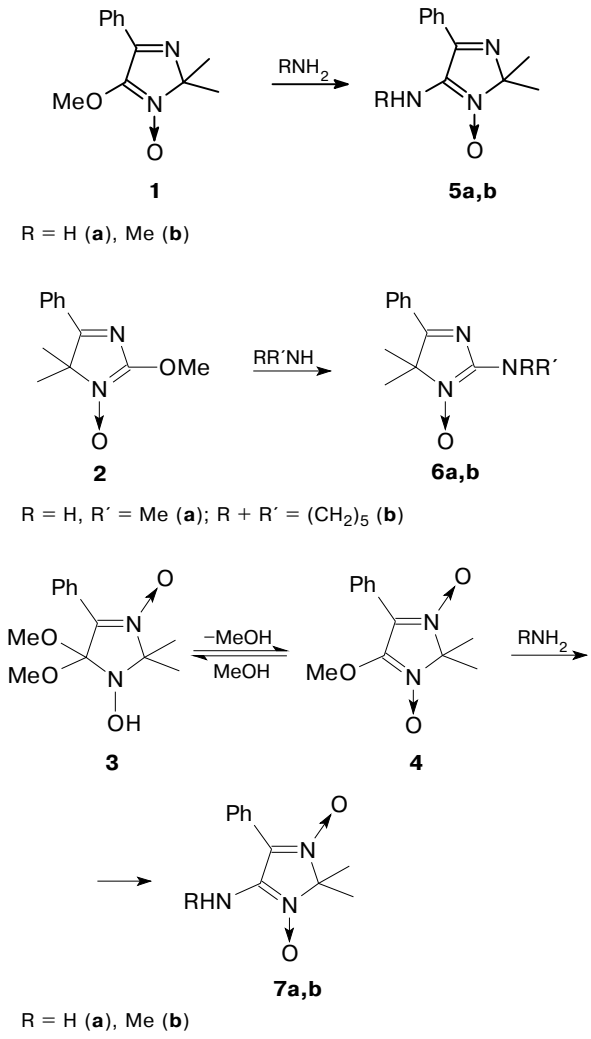
Key words: α-alkoxy nitrones (imidate *N*-oxides), nucleophilic substitution, cyclic α-amino nitrones, cyclic hydroxamic acids, cyclic thiohydroxamic acids, *2H*-imidazole *N*-oxides, *4H*-imidazole 3-oxides.

α-Alkoxy nitrones (imidate *N*-oxides) are difficultly accessible and generally unstable compounds. These compounds attract interest because of their high reactivity in nucleophilic substitution and 1,3-dipolar cycloaddition.[1—4] Recently,[5] we have reported a new procedure for the synthesis of *N*-oxides of 1,5-dihydro-2*H*-imidazole, 2*H*-imidazole, and 4*H*-imidazole containing the α-methoxy nitrone fragment in the ring. In the present work, we studied the reactions of these compounds with N-, O-, S-, and C-nucleophiles.

Previously,[2,6] we have demonstrated that the reactions of 4-methoxy-1,5-dihydro-2*H*-imidazole 3-oxides and acyclic α-methoxy nitrones with amines or ammonia resulted in the replacement of the methoxy group by the amino group to form the corresponding α-amino nitrones. Cyclic α-methoxy nitrones **1** and **2** and compound **3**, which (according to the NMR spectral data) exists in solutions in equilibrium with α-methoxy nitrone **4**,[5] behave analogously (Scheme 1). α-Amino nitrones **5a**,**b**, **6a**,**b**, and **7a**,**b** were isolated in the free state as crystalline yellow (**5** and **7**) or red (**6**) compounds. The IR spectra of these compounds have broad intense bands at 1680—1650 cm^{-1} characteristic of C=N stretching vibrations of α-amino nitrones.[2] Previously, it has been demonstrated[6] that the contribution of the hydroxylamino-imine tautomeric form in the case of α-amino nitrones is insignificant. Apparently, the chemical shifts of the carbon atoms of the N—C=N→O fragment in the ^{13}C NMR spectra of amino nitrone **6b** (δ 146.9) and compounds **5a**,**b**, **6a**, and **7a**,**b** capable of undergoing tautomerization (δ 142—151) indicate that these compounds also exist primarily as α-amino nitrones.

Unlike the reactions of acyclic α-methoxy nitrones and 4,5-dihydrooxazole *N*-oxides,[3,5,7] the reactions of compounds **1**, **2**, and **3** and 1,2,2,5,5-pentamethyl-4-methoxy-2,5-dihydroimidazole 3-oxide (**8**) with a solution of KOH in aqueous ethanol resulted in the forma-

Scheme 1



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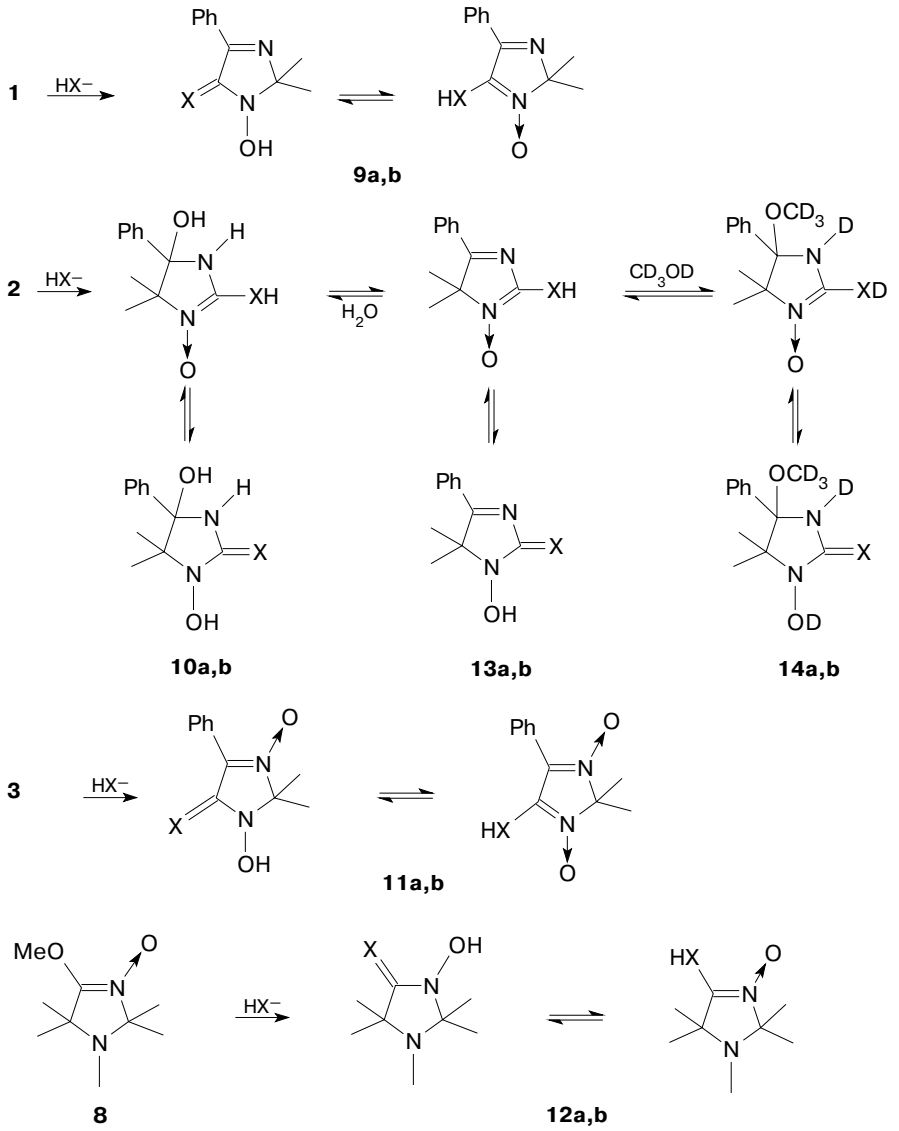
Scheme 2



tion of cyclic hydroxamic acids **9a—12a** rather than in the hydrolytic cleavage of the C=N bond (Scheme 2). The reactions of compounds **1**, **2**, **3**, and **8** with KSH gave analogous results, *viz.*, afforded thiohydroxamic acids **9b—12b**, respectively. Previously, compounds **12a**,**b** have been prepared from 4-cyano-1,2,2,5,5-pentamethyl-2,5-dihydroimidazole 3-oxide.[6,8]

Interestingly, the reactions of 4*H*-imidazole **2** with KOH or KSH were accompanied by the covalent hydration of the Ph—C=N bond. Analysis of the NMR spectra of the resulting 1,4-dihydroxy-5,5-dimethyl-4-phenylimidazolidin-2-one (**10a**) and -imidazolidine-2-thione (**10b**) demonstrated that these compounds, like 4-hydroxy-1-methoxy-5,5-dimethyl-4-phenylimidazolidin-2-one described previously,[5] reversibly eliminate the water molecule in CD_3OD solutions. The contents of 1-hydroxy-5,5-dimethyl-4-phenyl-2,5-dihydroimidazol-2(1*H*)-one (**13a**) and 1-hydroxy-5,5-dimethyl-4-phenyl-2,5-dihydroimidazole-2(1*H*)-thione (**13b**) in CD_3OD were ~5%. Storage of these solutions resulted in the replacement of the hydroxy group at position 4 of the heterocycle by the OCD_3 group to form compounds **14a,b**, respectively. The degree of conversion at 25 °C reached ~60% in 20 h.

For compounds **9—14**, tautomeric equilibrium (rapid within the NMR time scale) between α-hydroxy(α-mercapto) nitrones and hydroxamic (thiohydroxamic) acids can occur.[6] The chemical shifts of the carbonyl carbon atoms in the spectra of hydroxamic acids **9a**, **10a**, and **11a** (δ 158.49, 163.52, and 162.05, respectively) are very similar to those of the corresponding atoms in the spectra of fixed models, which cannot

undergo tautomerization, *viz.*, of methyl esters of the above-mentioned hydroxamic acids (δ 159.60, 164.43, and 163.91, respectively).[5] The signals for the carbon atoms of the —C=N→O group in the spectra of methoxy nitrones **1** and **2** are observed at δ 148.8 and 152.78, respectively. Therefore, the contribution of the α-hydroxy nitrone tautomeric form is insignificant, as in the case of 3-hydroxy-2,2,5,5-tetramethylimidazolidin-4-ones.[6]

For compounds **9b**, **10b**, **11b**, and **14b**, the tautomeric equilibrium is shifted to α-mercapto nitrone to a somewhat greater extent than in the case of compound **12b**.[6] In the ^{13}C NMR spectra of methanolic solutions of these compounds, the signals for the carbon atoms of the —C=N→O group are observed at δ 170.1, 183.4, 179.5, and 183.5, respectively, whereas the signals of the C=S groups of *N*-methoxy thioamides are observed at δ 190—195 and 137—148 for thiones and mercapto nitrones, respectively.[6] Therefore, the contribution of the tautomeric form of α-mercapto nitrone in CD_3OD can reach 20—40%.

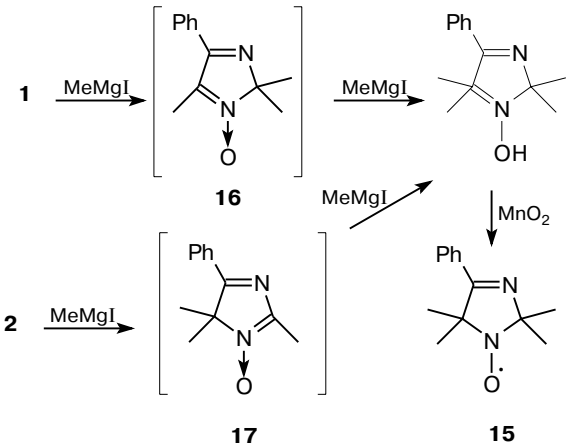
The reactions of cyclic α-alkoxy nitrones, which are dihydrooxazole or dihydrooxazine derivatives, with Grignard reagents are successfully used in the preparation of nitroxyl radicals, which are employed as spin probes.[9] The behavior of acyclic and cyclic α-methoxy nitrones under the action of organometallic compounds has not been studied previously.

The reactions of compounds **1** and **2** with an excess of methylmagnesium iodide followed by oxidation afforded the same nitroxyl radical, *viz.*, 2,2,5,5-tetramethyl-4-phenyl-2,5-dihydroimidazole-1-oxyl (**15**), in ~30% yield (Scheme 3). Apparently, the reactions proceeded through the formation of methylnitrones **16** and **17**, respectively. It is known[10] that the addition of organometallic compounds to 2,4,4-trimethyl-5-phenyl-4*H*-imidazole 3-oxide (**17**) occurs predominantly at position 2 of the heterocycle.

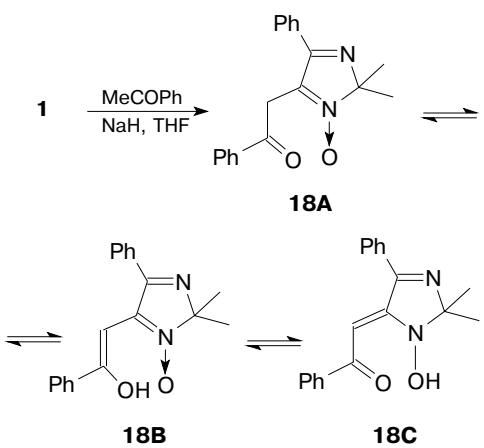
The reactions of α-alkoxy nitrones with enolate anions have not been studied previously. One would expect that these reactions will result in the replacement of the methoxy group to form either α-(β-hydroxyvinyl) nitrones or β-hydroxy nitrones (*N*-hydroxy enamino ketones). It is known that[11] hydroxy enamino ketones exist as a mixture of three tautomeric forms two of which give one set of signals in the NMR spectra due to the rapid intrachelate tautomerism.

We found that compound **1** readily entered into condensation with acetophenone in the presence of sodium hydride to form stable compound **18** existing as tautomeric forms **A**—**C** (Scheme 4). Colorless crystals (**18A**) slowly precipitated upon storage of yellow liquid samples of compound **18** or its solutions in diethyl ether. A yellow solution was again obtained after dissolution of these crystals. The UV spectrum of compound **18** in ethanol has a long-wavelength maximum at 390 nm, whereas the UV spectrum of a crystalline sample of **18A** in KBr has only a shoulder at 285 nm (in the region corresponding to absorption of 2*H*-imidazole 1-oxides[12]) and shows no absorption in the longer-wavelength region. The ^1H NMR spectra of compound **18** have two sets of signals. Their ratios in $(CD_3)_2CO$ and $(CD_3)_2SO$ are 2 : 1 and 3 : 2, respectively. The spectra of the major component have a singlet for two methylene protons at δ 4.59 and a singlet for the protons of the methyl groups at δ 1.49 (in the region characteristic of 2*H*-imidazole 1-oxides) along with a multiplet for the protons of the phenyl groups. The spectra of the minor component have a signal for the methine proton at δ 5.81. The signals for the protons of the geminal methyl groups are shifted downfield (δ 1.60) like in the spectra of dimethyl 2-(2,2-dimethyl-4-phenyl-1,5-dihydro-2*H*-imidazol-5-ylidene)-3-oxosuccinate,[13] hydroxamic acid **9a**, and its methyl ester.[5] From these data it follows that compound **18** is a mixture of tautomers, *viz.*, 5-benzoylmethyl-2,2-dimethyl-4-phenyl-2*H*-imidazole 1-oxide (**18A**), 4-(2-hydroxy-2-phenylvinyl)-2,2-dimethyl-5-phenyl-2*H*-imidazole 1-oxide (**18B**), and 5-benzoylmethylidene-1-hydroxy-2,2-dimethyl-4-phenyl-2,5-dihydro-1*H*-imidazole (**18C**).

Scheme 3



Scheme 4



Therefore, the behavior of cyclic α-methoxy nitrones in reactions with N-, O-, S-, and C-nucleophiles is analogous to the behavior of esters, *i.e.*, they give products of replacement of the methoxy group by the amino, hydroxy, or methoxy groups, enter into the Claisen condensation, and can add Grignard reagents at the carbon atom of the nitrone group.

Experimental

The IR spectra were recorded on Specord M-80 and Bruker IFS-66 spectrometers in KBr pellets (the concentration was 0.25%; the pellet thickness was 1 mm). The UV spectra were measured on a Specord M-40 spectrometer in ethanol. The spectral data are given in Table 1. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer for 1—5% solutions using the signal of the solvent as the standard (Table 2). The assignment of the signals in the ^{13}C NMR spectra was made based on analysis of intensities, on the spectra measured in the J-modulation mode, and using the data reported previously.[5,6] Column chromatography was carried out on silica gel Kieselgel 60 (Merck).

Synthesis of amino nitrones 5a,b—7a,b. A saturated solution of amine in MeOH (10 mL) was added to a solution of α-methoxy nitrones **1—3** (2 mmol) in MeOH (2 mL). After the starting compound was consumed (TLC control), the solvent was evaporated *in vacuo*. Analogously, the addition of piperidine to a methanolic solution of compound **2** afforded **4,4-dimethyl-5-phenyl-2-piperidino-4*H*-imidazole 3-oxide (6b)**. **5-Amino-2,2-dimethyl-4-phenyl-2*H*-imidazole 1-oxide (5a)** and **5-amino-2,2-dimethyl-4-phenyl-2*H*-imidazole 1,3-dioxide (7a)** were recrystallized from acetone. **5-Methylamino-2,2-dimethyl-4-phenyl-2*H*-imidazole 1-oxide (5b)** was recrystallized from ethyl acetate. **5-Methylamino-2,2-dimethyl-4-phenyl-2*H*-imidazole 1,3-dioxide (7b)** was recrystallized from a 2 : 1 ethyl acetate—hexane mixture. **2-Methylamino-4,4-dimethyl-5-phenyl-4*H*-imidazole 3-oxide (6a)** and **4,4-dimethyl-5-phenyl-2-**

Table 1. Characteristics of the compounds synthesized

Compound	Yield (%)	M.p./°C	Found / Calculated (%)			Molecular formula	IR spectrum (in KBr), ν/cm^{-1}	UV spectrum (EtOH), λ_{max}/nm (log ε)
			C	H	N			
5a	90	185—187	62.2 62.3	6.6 6.6	19.6 19.8	$C_{11}H_{13}N_3O \cdot 0.5\ H_2O$	1670 (N—C=N); 1550 (C=N)	218 (4.54); 242 (4.52)
5b	85	143—145	66.3 66.4	7.1 6.9	19.4 19.4	$C_{12}H_{15}N_3O$	1675 (N—C=N); 1560 (C=N)	248 (4.23); 360 (3.70)
6a	90	175—179	63.6 63.7	7.0 7.1	18.5 18.6	$C_{12}H_{15}N_3O \cdot 0.5\ H_2O$	1670 (N—C=N)	245 (3.82); 273 (3.92); 409 (3.34)
6b	40	147—149	68.6 68.5	7.6 7.9	15.1 15.0	$C_{16}H_{21}N_3O \cdot 0.5\ H_2O$	1630 (N—C=N)	271 (4.29); 510 (3.69)
7a	85	157—160	60.4 60.3	6.3 5.9	18.8 19.2	$C_{11}H_{13}N_3O_2$	1670 (N—C=N); 1550 (C=N)	250 (4.11); 293 (3.58); 391 (3.23)
7b	70	151—153	61.7 61.8	6.5 6.4	18.0 18.0	$C_{12}H_{15}N_3O_2$	1660 (N—C=N); 1530 (C=N)	227 (3.54); 252 (4.04); 285 (4.00); 398 (3.26)
9a	95	81—84	64.5 64.7	5.9 5.9	13.6 13.7	$C_{11}H_{12}N_2O_2$	1725 (C=O); 1590 (C=N)	262 (4.18)
9b	65	114—117	59.6 60.0	5.4 5.5	12.5 12.7	$C_{11}H_{12}N_2OS$	1610 (C=N)	242 (4.00); 272 (3.93)
10a	40	127—129	55.4 55.0	6.8 6.7	11.7 11.7	$C_{11}H_{14}N_2O_3 \cdot H_2O$	1722 (C=O); 3381 (OH)	263.2 (2.96)
10b[a]	90	84—87	53.4 53.4	6.0 6.1	11.3 11.3	$C_{11}H_{14}N_2O_2S \cdot 0.5\ H_2O$	3580, 3480 (OH)	250 (KBr); 251 (4.20); 295 sh[b] (3.94)
11a	90	143—146	60.4 60.0	5.7 5.5	12.7 12.7	$C_{11}H_{12}N_2O_3$	1717(C=O); 1550 (C=N)	231 (4.18); 285 (4.01)
11b	85	137—140	55.6 55.9	5.1 5.1	11.6 11.9	$C_{11}H_{12}N_2O_2S$	1550 (C=N)	334.6 (4.23); 334.1 (4.10)[c]
18	65	92—95	75.0 74.5	6.1 5.9	9.0 9.2	$C_{19}H_{18}N_2O_2$	1691 (C=O); 1594, 1596 (C=N); 1730[d], 1695 (C=O)[d]; 1606[d], 1573 (C=N)[d]	237 (KBr); 285 sh[b] (KBr); 390 (3.66); 276 (4.23); 241 (4.32)

[a] Found (%): S, 12.6. Calculated (%): S, 12.9.
[b] Shoulder.
[c] Heptane as the solvent.
[d] In CCl_4.

Table 2. Data of ^1H and ^{13}C NMR spectroscopy of the compounds synthesized

Compound	Solvent	δ (*J*/Hz)	
		^1H	^{13}C
5a	CD_3OD	1.61 (s, 6 H, *gem*-Me); 7.63, 7.86 (both m, 3 H and 2 H, N=C—Ph)	23.81 (*gem*-Me); 94.40 ($\underline{C}Me_2$); 143.06 (NH_2—C=N); 161.82 (Ph—C=N); Ph: 131.81 (C_i); 128.82 (C_o); 130.21 (C_m); 132.90 (C_p)
5b	CD_3OD	1.60, 1.61 (both s, 3 H each, *gem*-Me); 3.18 (c, 3 H, NH—Me); 7.61, 7.70 (both m, 3 H and 2 H, N=C—Ph)	23.91 (*gem*-Me); 29.93 (N—Me); 94.70 ($\underline{C}Me_2$); 142.86 (NH_2—C=N); 165.52 (Ph—C=N); Ph: 132.31 (C_i); 129.02 (C_o); 130.11 (C_m); 132.53 (C_p)
6a	$CDCl_3$	1.64 (s, 6 H, *gem*-Me); 3.19 (c, 3 H, NH—Me); 7.48, 7.97 (both m, 3 H and 2 H, N=C—Ph)	21.91 (*gem*-Me); 25.79 (N—Me); 75.07 ($\underline{C}Me_2$); 150.81 (N—C=N); 182.08 (Ph—C=N); Ph: 129.98 (C_i); 127.68 (C_o); 128.86 (C_m); 132.24 (C_p)
6b	$(CD_3)_2CO$ (^1H); $(CD_3)_2SO$ (^{13}C)	1.55 (s, 6 H, *gem*-Me); 1.58; 3.93 (both m, 6 H and 4 H, piperidyl); 7.50, 8.03 (both m, 3 H and 2 H, N=C—Ph)	23.2 (*gem*-Me); 24.0; 25.6; 46.2 (piperidyl); 76.6 ($\underline{C}Me_2$); 146.9 (N—C=N); 177.9 (Ph—C=N); Ph: 129.7 (C_i); 127.4 (C_o); 129.1 (C_m); 132.0 (C_p)
7a	CD_3OD	1.79 (s, 6 H, *gem*-Me); 7.61, 7.96 (both m, 3 H and 2 H, N=C—Ph)	23.81 (*gem*-Me); 94.26 ($\underline{C}Me_2$); 144.87 (N—C=N); 132.95 (Ph—C=N); Ph: 124.91 (C_i); 132.44 (C_o); 129.60 (C_m); 130.00 (C_p)
7b	CD_3OD	1.79 (s, 6 H, *gem*-Me); 3.13 (s, 3 H, NH—Me); 7.61, 7.71 (both m, 3 H and 2 H, N=C—Ph)	23.95 (*gem*-Me); 30.99 (N—Me); 94.43 ($\underline{C}Me_2$); 144.49 (N—C=N); 134.38 (Ph—C=N); Ph: 125.01 (C_i); 130.07 (C_o); 130.44 (C_m); 132.37 (C_p)
9a	CD_3OD	1.57 (s, 6 H, *gem*-Me); 7.53, 8.34 (both m, 3 H and 2 H, N=C—Ph)	24.30 (*gem*-Me); 84.43 ($\underline{C}Me_2$); 158.49 (C=O); 163.12 (P—C=N); Ph: 132.01 (C_i); 128.91 (C_o); 129.64 (C_m); 132.00 (C_p)
9b	CD_3OD	1.63 (s, 6 H, *gem*-Me); 7.52, 8.34 (both m, 3 H and 2 H, N=C—Ph)	23.70 (*gem*-Me); 93.50 ($\underline{C}Me_2$); 170.12 (C=S); 165.51 (Ph—C=N); Ph: 133.11 (C_i); 128.98 (C_o); 130.40 (C_m); 132.32 (C_p)
10a	CD_3OD	0.72, 1.43 (both s, 3 H each, *gem*-Me); 7.40, 7.56 (both m, 3 H and 2 H, Ph)	18.71, 20.87 (*gem*-Me); 69.98 ($\underline{C}Me_2$); 93.51 (Ph—C—N); 163.52 (C=O); Ph: 141.05 (C_i); 127.71 (C_o); 128.11 (C_m); 129.82 (C_p)
10b	CD_3OD	0.72, 1.47 (both s, 3 H each, *gem*-Me); 7.43, 7.55 (both m, 3 H and 2 H, Ph)	18.15, 21.32 (*gem*-Me); 72.94 ($\underline{C}Me_2$); 91.52 (Ph—C—N); 183.42 (C=S); Ph: 140.13 (C_i); 127.44 (C_o); 128.14 (C_m); 129.52 (C_p)
11a	CD_3OD	1.73 (s, 6 H, *gem*-Me); 7.53, 8.67 (both m, 3 H and 2 H, N=C—Ph)	23.84 (*gem*-Me); 99.37 ($\underline{C}Me_2$); 140.45 (Ph—C=N); 162.05 (C=O); Ph: 127.15 (C_i); 128.73 (C_o); 129.27 (C_m); 132.17 (C_p)
11b	CD_3OD	1.78 (s, 6 H, *gem*-Me); 7.50, 8.24 (both m, 3 H and 2 H, N=C—Ph)	23.40 (*gem*-Me); 93.84 ($\underline{C}Me_2$); 138.76 (Ph—C=N); 179.48 (C=S); Ph: 126.78 (C_i); 128.66 (C_o); 131.07 (C_m); 131.68 (C_p)
13a	CD_3OD	1.68 (s, 6 H, *gem*-Me)	23.91 (*gem*-Me)
13b	CD_3OD	1.70 (s, 6 H, *gem*-Me); 7.60, 8.20 (both m, 3 H and 2 H, N=C—Ph)	22.77 (*gem*-Me); 77.01 ($\underline{C}Me_2$)
14a	CD_3OD	0.69, 1.42 (both s, 3 H each, *gem*-Me); 7.47 (m, 5 H, Ph)	18.37, 20.74 (*gem*-Me); 70.8 ($\underline{C}Me_2$); 93.50 (Ph—C—N); 163.82 (C=O); Ph: 137.54 (C_i); 128.46 (C_o); 129.51 (C_m); 129.82 (C_p)
14b	CD_3OD	0.67, 1.44 (both s, 3 H each, *gem*-Me); 7.46 (m, 5 H, Ph)	17.78, 21.05 (*gem*-Me); 74.01 ($\underline{C}Me_2$); 95.64 (Ph—C—N); 183.50 (C=S); Ph: 136.48 (C_i); 128.21 (C_o); 129.54 (C_m); 130.00 (C_p)
18A	$(CD_3)_2SO$	1.49 (s, 6 H, *gem*-Me); 4.59 (s, 2 H, CH_2); 7.41—7.99 (m, 10 H, 2 Ph)	
18B (18C)	$(CD_3)_2SO$	1.60 (s, 6 H, *gem*-Me); 5.81 (s, H, CH); 7.41—7.99 (m, 10 H, 2 Ph)	

piperidino-4*H*-imidazole 3-oxide (6b) were isolated by chromatography on SiO_2 with the use of the 10 : 1 $CHCl_3$—MeOH mixture as the eluent and recrystallized from hexane.

Synthesis of hydroxamic (9a—12a) and thiohydroxamic acids (9b—12b). A solution of KOH (4 mmol) in aqueous methanol (5 mL) or a solution of KSH (5 mmol) in MeOH (2 mL) was added to a solution of α-methoxy nitrone (**1**—**3** or **8**; 2 mmol) in MeOH (2 mL). After the starting compound was consumed (TLC control, Silufol UV-254, $CHCl_3$—MeOH, 50 : 1), the solvent was evaporated *in vacuo*. Water (10 mL) was added to the residue. The resulting solution was washed with *tert*-butyl methyl ether and acidified with 10% HCl to pH 5. The product was extracted with $CHCl_3$. The extract was dried with Na_2SO_4, the solvent was evaporated, and the residue was recrystallized. **1-Hydroxy-2,2-dimethyl-4-phenyl-1,2-dihydroimidazol-5-one (9a)** was recrystallized from the 4 : 1 hexane—acetone

mixture. **1-Hydroxy-2,2-dimethyl-4-phenyl-1,2-dihydroimidazole-5-thione (9b)** was recrystallized from the 2 : 1 ethyl acetate—hexane mixture. **1-Hydroxy-2,2-dimethyl-4-phenyl-1,2-dihydroimidazol-5-one 3-oxide (11a)** and **1-hydroxy-2,2-dimethyl-4-phenyl-1,2-dihydroimidazole-5-thione 3-oxide (11b)** were recrystallized from ethyl acetate. **1,4-Dihydroxy-5,5-dimethyl-4-phenylimidazolidin-2-one (10a)** and **1,4-dihydroxy-5,5-dimethyl-4-phenylimidazolidine-2-thione (10b)** were recrystallized from water. **3-Hydroxy-1,2,2,5,5-pentamethylimidazolidin-3-one (12a)** and **3-hydroxy-1,2,2,5,5-pentamethylimidazolidine-3-thione (12b)** were isolated as described previously.[6,8]

Reactions of compounds 1 and 2 with MeMgI. A solution of α-methoxy nitrone **1** or **2** (0.3 g, 1.4 mmol) in THF (10 mL) was added dropwise with stirring to a solution of MeMgI, which has been prepared from Mg (100 mg, 4 mg-at.), MeI (0.6 g), and diethyl ether (20 mL). The reaction mixture was stirred at ~20 °C for 1 h and quenched with water (15 mL). The organic phase was separated and the aqueous solution was extracted with *tert*-butyl methyl ether (3×15 mL). Then MnO_2 (1 g) and anhydrous $MgSO_4$ (1 g) were added to the combined extracts. The mixture was stirred for 2 h and filtered. The solvent was evaporated *in vacuo* and the residue was chromatographed on a column with SiO_2 using $CHCl_3$ as the eluent. The nitroxyl radical **2,2,5,5-tetramethyl-4-phenyl-2,5-dihydro-1*H*-imidazole-1-oxyl (15)** was obtained in yields of 95 and 85 mg in the case of compounds **1** and **2**, respectively, m.p. 79—80 °C. The IR spectra of the resulting samples were identical with the spectrum published previously.[14]

5-Benzoylmethyl-2,2-dimethyl-4-phenyl-2*H*-imidazole 1-oxide (18). A solution of α-methoxy nitrone **1** (450 mg, 2 mmol) and acetophenone (0.3 mL, 2.5 mmol) in THF (5 mL) was added dropwise with stirring to a suspension of 60% sodium hydride (170 mg, 4 mmol) in dry THF (5 mL). The reaction mixture was stirred at ~20 °C for 4 h and quenched with AcOH (1 mL) and water (10 mL). Then the reaction mixture was extracted with *tert*-butyl methyl ether (3×10 mL), the extract was dried with $MgSO_4$, the solvent was evaporated, and the reside was chromatographed on a column with silica gel using $CHCl_3$ as the eluent.

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