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ESR Evidence for the Stereospecific Spin Trapping of 5-Alkyl-5-Methyl-1-Pyrroline *N*-oxides

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The ability of ten cyclic nitrones, 5-alkyl-5-methyl-1-pyrroline *N*-oxides, to trap a variety of short-lived free radicals has been investigated using ESR spectroscopy. Stereospecific spin trapping by these nitrones has been demonstrated by comparison of the ESR spectra of their adducts with the ESR spectra of the corresponding 5-alkyl-5-methyl-1-tetrahydropyrrolyl-1-oxyls. Phenyl radical *trans* addition to these nitrones has also been proved.

KEY WORDS ESR Spin trapping Stereospecificity Cyclic nitrone Free radical

INTRODUCTION

It is well known that short-lived free radicals play an important role in many chemical and biological processes, and they can be detected and identified by spin trapping techniques.[1,2] The most important question, however, is how to select a suitable spin trap for a particular problem. A cyclic nitrone, 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), has been widely used as a spin trap for active free radicals.[3–6] Owing to the superior spin trapping properties of DMPO, many DMPO analogues with long alkyl chains[7–9] have recently been synthesized to study radicals in biological systems. However, the introduction of one long alkyl chain at the C-5 position of the pyrroline ring poses a stereochemical problem with the spin trapping process. Although five 5-alkyl-5-methyl-1-pyrroline *N*-oxides have been used to trap the *tert*-butoxyl radical,[7] $O_2^{\cdot -}$ and hydroxyl radicals,[10] the ability to trap other radicals and the stereochemical consequences of trapping with these nitrones have not previously been examined.

In order to resolve these important and interesting problems, ten 5-alkyl-5-methyl-1-pyrroline *N*-oxides, in which the alkyl groups are *n*-hexadecyl, *n*-tetradecyl, *n*-dodecyl, *n*-decyl, *n*-nonyl, *n*-octyl, *n*-hexyl, *n*-pentyl, *n*-butyl or *n*-propyl, have been synthesized in our laboratory using 2-methyl-1-pyrroline *N*-oxide (MPO) and the corresponding Grignard reagents as starting materials by the method reported in the literature[11] (Scheme 1). Their ability to trap a number of free radicals has been investigated by ESR spectroscopy. The stereospecificity of trapping with these nitrones has also been demonstrated.

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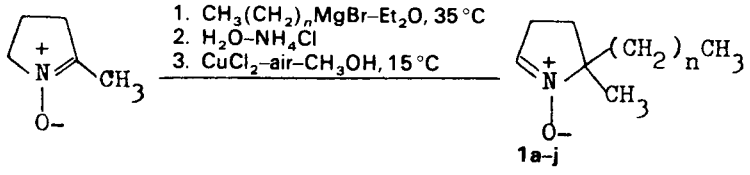
RESULTS AND DISCUSSION

Spin trapping test

The hyperfine splitting constants (h.f.s.c.) of spin adducts from nitrones **1a–j** are listed in Table 1. The spin trapping results indicate that these nitrones can effectively trap many types of C- and O-centred radicals, for example, $C_6H_5^{\cdot}$, $HOCH_2^{\cdot}$, $CH_3\dot{C}HOH$, $C_2H_5\dot{C}HOH$, $(CH_3)_2\dot{C}OH$, $(CH_3)_2\dot{C}CN$, $C_2H_5O\dot{C}HCH_3$, tetrahydrofuranyl, dioxanyl and *tert*-butoxyl. They can trap both radicals produced by the photolysis of some compounds such as Ph_3Sb, azobisisobutyronitrile (AIBN) and *tert*-dibutyl peroxide, and radicals formed in photochemical reaction systems such as triplet benzophenone with alcohols or ethers. The spin adduct is stable, so these nitrones can be used to trap radicals produced by the thermolysis of AIBN at 80 °C in benzene. It should be noted that each radical reacts with these nitrones to give spin adducts with essentially the same spectra, i.e. the length of the alkyl



1	a	b	c	d	e	f	g	h	i	j
n =	15	13	11	9	8	7	5	4	3	2

Scheme 1

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Table 1. ESR parameters for spin adducts in gauss

Spin trap	Radical: Ph·[a] a_N	a_H^β	a_H^γ	$HO\dot{C}H_2$[b] a_N	a_H^β	a_H^γ	$CH_3\dot{C}HOH$[b] a_N	a_H^β	a_H^γ	$C_2H_5\dot{C}HOH$[b] a_N	a_H^β	a_H^γ
1a	13.3	20.0		13.9	21.5		14.0	22.3		14.1	22.4	
1b	13.8	19.3		14.5	21.8		14.1	22.5		14.1	22.4	
1c	13.7	20.6		14.9	22.1		14.5	22.9		14.7	23.3	
1d				14.8	22.3		14.6	22.7		14.7	22.9	
1e				14.6	22.1		14.6	23.1		14.6	23.1	
1f	13.6	20.1		14.6	22.2		14.5	23.0		14.8	23.3	
1g				14.6	22.1		14.7	23.4		14.9	23.3	
1h	13.6	20.1		14.7	22.2		14.7	23.1		14.7	23.1	
1i				14.6	22.0		14.6	23.1		14.6	22.9	
1j	13.7	20.6					14.7	23.2		14.7	23.2	

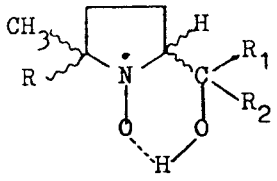
	Radical: $(CH_3)_2\dot{C}OH$[b] a_N	a_H^β	a_H^γ	$C_2H_5O\dot{C}HCH_3$[c] a_N	a_H^β	a_H^γ	Tetrahydrofuranyl[c] a_N	a_H^β	a_H^γ	Dioxanyl[c] a_N	a_H^β	a_H^γ
1a	13.8	23.7		13.9	20.8		13.3	18.3				
1b	13.9	23.9		13.5	20.0		13.6	18.5				
1c	14.4	24.7		13.5	20.2		14.0	19.0		13.9	19.4	
1d				13.8	20.7		13.9	19.2				
1e				13.9	20.8		13.8	18.9				
1f				13.8	20.7		13.9	19.0		13.7	19.3	
1g				13.9	20.8		13.8	18.6				
1h				13.9	20.7		13.9	18.9				
1i	14.5	24.4		13.8	21.0		13.9	19.0		14.0	19.4	
1j				13.9	21.2		13.9	18.9				

	Radical: $(CH_3)_3CO\cdot$ a_N	a_H^β	a_H^γ	$(CH_3)_2\dot{C}CN$ a_N	a_H^β	a_H^γ
1a	12.5	7.9	1.4[d] (1H)	12.0	7.9	1.6[f] (1H)
	12.2	8.0[e]		12.1	8.2	1.6[g] (1H)
1b	12.4	7.8	1.6[d] (1H)	12.3	8.2	1.4[f] (1H)
	12.2	7.4	1.6[e] (1H)	11.9	7.9	1.7[g] (1H)
1c	13.0	8.2	1.8[d] (1H)	12.6	8.6	1.6[f] (1H)
1d				12.7	8.7	1.6[f] (1H)
1e	13.2	8.0	1.9[d] (1H)	12.6	8.6	1.6[f] (1H)
1f				12.6	8.7	1.9[f] (1H)
1g				12.4	8.4	1.7[f] (1H)
1h	13.3	7.7	1.9[d] (1H)	12.5	8.0	1.9[f] (1H)
1i				12.5	8.5	1.8[f] (1H)

[a] Photolysis of Ph_3Sb in benzene with a 200-W high-pressure mercury lamp.
[b] Photolysis of ROH in the presence of benzophenone in benzene.
[c] Photolysis of ether in benzene.
[d] Photolysis of di-*tert*-butyl peroxide in benzene.
[e] Obtained by the reaction of *tert*-BuOOH with $K_4Fe(CN)_4$.
[f] Photolysis of AIBN in benzene.
[g] Thermolysis of AIBN at 80 °C in benzene.

chains at the C-5 position of the pyrroline ring has little influence on the h.f.s.c. values of the spin adducts. The ESR spectra of these nitrone adducts are sensitive to the nature of the radicals, in a similar manner to the DMPO adducts.[5] The relatively larger h.f.s.c. values for the hydroxyalkyl spin adducts of these ten nitrones may be due to an increase in spin density on nitrogen and a decrease in the β-CH dihedral angle, caused by intramolecular hydrogen bonding from the hydroxy hydrogen to the nitroxyl oxygen[5,12] (Scheme 2).

The addition of phenyl, hydroxyalkyl, 1-ethoxy-1-ethyl, tetrahydrofuranyl, dioxanyl or *tert*-butoxyl radicals to these nitrones give spin adducts whose h.f.s.c. values are in agreement with those of the DMPO



Scheme 2

adducts.[7] The h.f.s.c. values for 2-cyano-2-propyl adducts, however, are very different from that of the DMPO adduct. In contrast to the larger hydrogen h.f.s.c. (a_H^{β}) reported for DMPO,[5,9] the 2-cyano-2-propyl spin adducts of nitrones **1a–j** show abnormally lower a_H^{β} values. This phenomenon has also been observed when trapping this radical with 5-alkyl-3,3,5-trimethyl-1-pyrroline *N*-oxides (ATMPO).[11] In contrast to ATMPO adducts, all of the **1a–f** adducts with this radical show h.f.s.c. values for the γ-hydrogen (a_H^{γ}), which indicates that both the large 2-cyano-2-propyl group and a long alkyl substituent may change the conformational structure of the tetrahydropyrrole ring to cause a decrease in the β-CH dihedral angle and an increase in the interaction between the γ-hydrogen and an odd electron.

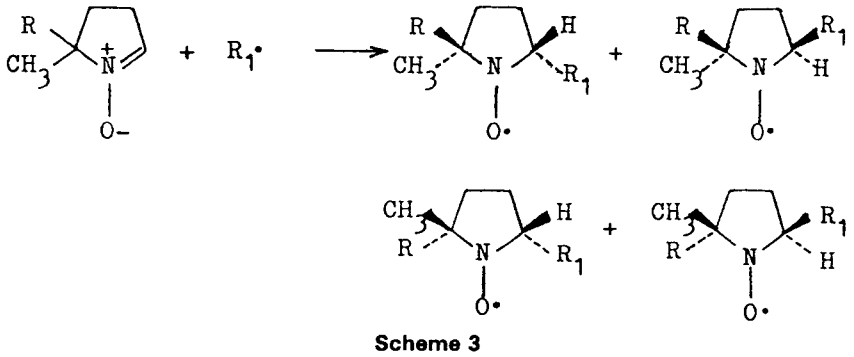
Stereochemistry

It should be noted that there is a C-5 chiral carbon in each of the nitrones **1a–j**. Because every nitrone reported in this paper is a racemic mixture, there are four possible isomeric spin adducts of the spin trapping reaction (Scheme 3). *trans*- And *cis*-adducts should show different a_H^{β} values since their C-β—H bonds have different orientations with respect to the semi-occupied *p*-orbital of the nitrogen atom.[9] This hypothesis can be substantiated as follows. Each of these ten nitrones was reduced with $LiAlH_4$ in absolute diethyl ether for 1 h; a small amount of water was then added to decompose excess of $LiAlH_4$. The diethyl ether was removed, the aqueous solution extracted with benzene and then finally oxidized in air[13,14] to give the corresponding tetrahydropyrrolyl-1-oxyl radical (Scheme 4). All the ESR spectra of nitroxides **2a–j** show a doublet of doublet of triplet signals, as shown in Fig. 1. DMPO was treated by the same procedure to give dimethyltetrahydropyrrolyl-1-oxyl (DTPO), which shows triplet of triplet signals. These results indicate that two β-hydrogens in each of **2a–j** are magnetically non-equivalent. The ten ESR h.f.s.c. values of **2a–j** and DTPO are given in Table 2.

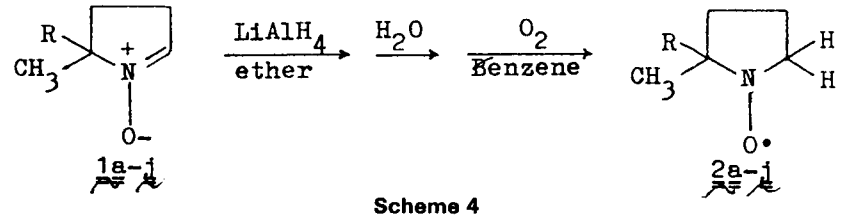
Table 2. ESR hyperfine splitting constants of nitroxides 2a–j and DTPO

Nitroxide	a_N (G)	a_H^{β} (G)	a_H^{β} (G)
2a	13.8	19.3	17.4
2b	13.9	19.2	17.5
2c	13.8	19.1	17.5
2d	14.1	19.7	17.8
2e	14.4	19.8	18.0
2f	14.4	20.0	18.2
2g	14.2	19.7	17.9
2h	14.3	19.9	18.1
2i	14.4	20.0	18.1
2j	14.4	20.0	18.2
DTPO	14.5	19.0	19.0

The reason for two magnetically nonequivalent β-hydrogens is probably that the larger substituent in each of **2a–j** tends to take the pseudo-equatorial position in the preferential conformation at room temperature; the β-hydrogen *trans* to the larger substituent is in the pseudo-axial position and its orientation with respect to the semi-occupied *p*-orbital of nitrogen is different from that of the β-hydrogen which is *cis* to the larger substituent. For the same reason the β-hydrogen in the *trans* adduct should be magnetically different from that in the *cis* adduct, and different h.f.s.c. values should be shown in the ESR spectrum if *trans* and *cis*



Scheme 3



Scheme 4

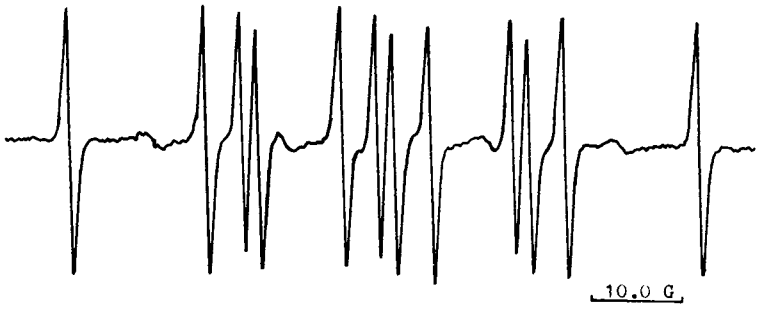


Figure 1. ESR spectrum of nitroxide **2f** in benzene at room temperature.

adducts are generated in the course of the same spin trapping reaction.

However, only one a_N and one a_H^β value (Table 1) is obtained in the ESR spectrum when each of the nitrones **1a–j** traps some of the radicals. These spin trapping reactions are therefore stereospecific, or the stereoselectivity is so high that other spin adducts cannot be detected by ESR. Considering that the steric hindrance of an alkyl group, such as *n*-propyl, is greater than that of the methyl group, free radicals should add to nitrones **1a–j** from the direction which is *trans* to the larger substituent to offer *trans* adducts. It has been reported that this type of nitrone reacts with Grignard reagents and alkyllithiums to give preferentially the *trans* isomers.[11,15,16] This result is used in this paper to demonstrate that the addition of radicals to these nitrones also gives *trans* adducts. Nitrone **1f** was reacted with phenylmagnesium bromide to give 2-phenyl-5-*n*-octyl-5-methyltetrahydropyrrolyl-1-hydroxyl, which was characterized by its mass spectrum. Oxygen was bubbled through a benzene solution of this hydroxylamine to provide the corresponding nitroxide. The ESR spectrum shows that the h.f.s.c. values of *trans* adducts are $a_N = 13.8$ G and $a_H^\beta = 20.5$ G, and those of *cis* adducts are $a_N = 13.8$ G and $a_H^\beta = 24.8$ G. The ratio of the ESR peak heights of the *trans* adducts to those of the *cis* adducts is approximately 5.5:1, and after standing for 5 h the ratio became *ca.* 2:1. This result indicates that *trans* adducts are less stable than the *cis* adducts. It can thus be concluded that one of the two large groups, i.e. *n*-octyl or phenyl, is in a pseudo-axial position in the preferential conformation of *trans* adducts, whereas the two larger groups are both in pseudo-equatorial positions in the *cis* adducts. When nitrone **1f** traps phenyl radicals, the ESR spectrum shows $a_N = 13.6$ G and $a_H^\beta = 20.1$ G for the adduct. These parameters are consistent with the h.f.s.c. values for *trans* adducts, and are substantially different from those of *cis* adducts. Similarly, the ESR parameters for *trans* adducts from nitrone **1j** and phenylmagnesium bromide are $a_N = 14.0$ G and $a_H^\beta = 20.9$ G, which is also consistent with $a_N = 13.7$ G and $a_H^\beta = 20.6$ G for the spin adducts from nitrone **1j** and phenyl radicals. Therefore, it could be concluded that the addition reaction of phenyl radicals with each nitrone **1a–j** is stereospecific, and *trans* adducts are produced. It may be predicted that other radicals, such as hydroxyalkyl, tetrahydrofuranyl, 1-ethoxy-1-ethyl, dioxanyl, *tert*-butoxy and 2-cyano-2-propyl, probably add to nitrones **1a–j** from the direction *trans* to the larger substituent to give *trans* adducts.

CONCLUSION

5-Alkyl-5-methyl-1-pyrroline *N*-oxides are effective spin traps for C- and O-centred radicals. The ESR spectra of spin adducts are sensitive to the nature of every scavenged radical. Two β-hydrogens in nitroxides 5-alkyl-5-methyltetrahydropyrrolyl-1-oxyls are magnetically nonequivalent. Addition reactions of phenyl, hydroxyalkyl, 1-ethoxy-1-ethyl, tetrahydrofuranyl, dioxanyl, *tert*-butoxyl and 2-cyano-2-propyl to these nitrones are stereospecific; in other words, the stereoselectivity is so high that other adducts cannot be detected by ESR spectroscopy. These ten nitrones trap phenyl radicals to give *trans* adducts. Other radicals should also give *trans* adducts, although exceptions might exist.

EXPERIMENTAL

The starting material, 2-methyl-1-pyrroline *N*-oxide (MPO), was prepared by a procedure described in the literature.[17] The alkyl bromides, which were distilled before use, and the magnesium powder were purchased from the Beijing Chemical Factory. Preparative thin-layer chromatographic plates were made in our laboratory by the standard method. DMPO was prepared according to a literature method.[18] Nitroxides **2a–j** and DTPO are unstable because of the existence of β-hydrogens and were measured directly by ESR.

Melting points are uncorrected. Microanalyses were obtained using a Heraeus-CHN-Rapid elemental analyser. IR spectra were recorded on a Carl Zeiss Jena Specord-75 spectrometer. Mass spectra were obtained using an AEI MS-50/DS-30 spectrometer. ^{1}H NMR spectra were determined on Varian EM-360 (60 MHz) and Bruker AC-80 (80 MHz) spectrometers. ESR spectra were recorded on a Bruker EPS-300 ESR spectrometer, in benzene solution at room temperature.

5-*n*-Hexadecyl-5-methyl-1-pyrroline *N*-oxide (1a)

The procedure used in the literature[13] was adapted, and a six-fold ratio of hexadecylmagnesium bromide, which was freshly prepared, to the nitrone MPO was used. The crude product was chromatographed on a silica gel column eluted with dichloromethane, tetrahydrofuran and ethanol, successively, and further purified by preparative thin-layer chromatography to give a slightly yellowish solid which was dried at 78 °C/10 mmHg for

12 h in the presence of P_2O_5. Yield, 48%; m.p., 40–41 °C; IR, ν 2916, 2849, 1575, 1457, 1225; ^{1}H NMR ($CDCl_3$/TMS), δ 0.88 (t, 3H), 1.26 (s, 28H), 1.40 (s, 3H), 1.5–1.9 (m, 2H), 1.9–2.3 (m, 2H), 2.3–2.8 (m, 2H), 6.85 (br., 1H); MS, *m/z* 323.3185 (calculated for $C_{21}H_{41}NO$, 323.3189), 306, 140, 126, 99, 98, 82. Analysis: calculated for $C_{21}H_{41}NO$, C 77.96, H 12.77, N 4.32; found, C 77.16, H 12.59, N 4.00%.

5-*n*-Tetradecyl-5-methyl-1-pyrroline *N*-oxide (1b)

This compound was prepared by a similar procedure to that used for **1a**. Yield, 73%; m.p., 34–35 °C; IR, ν 2913, 2843, 1579, 1460, 1225; ^{1}H NMR ($CDCl_3$/TMS), δ 0.88 (t, 3H), 1.26 (s, 24H), 1.40 (s, 3H), 1.6–1.9 (m, 2H), 1.95–2.3 (m, 2H), 2.4–2.7 (m, 2H), 6.82 (t, 1H, J = 2.2–2.6 Hz); MS, *m/z* 295.2872 (calculated for $C_{19}H_{37}NO$, 295.2875), 278, 140, 126, 99, 98, 82, 81. Analysis; calculated for $C_{19}H_{37}NO$ + 3/5 H_2O, C 74.50, H 12.57, N 4.57; found, C 74.32, H 12.25, N 4.74%.

5-*n*-Dodecyl-5-methyl-1-pyrroline *N*-oxide (1c)

This compound was prepared by a similar procedure to that used for **1a**. Yield, 59%; m.p., 26.5–29 °C; IR, ν 2925, 2852, 1575, 1460, 1233; ^{1}H NMR ($CDCl_3$/TMS), δ 0.89 (t, 3H), 1.26 (s, 20H), 1.41 (s, 3H), 1.6–1.9 (m, 2H), 1.96–2.3 (m, 2H), 2.4–2.7 (m, 2H), 6.83 (t, 1H); MS, *m/z* 267.2562 (calculated for $C_{17}H_{33}NO$, 267.2562), 250, 140, 126, 114, 99, 98, 82, 81. Analysis: calculated for $C_{17}H_{33}NO$ + 1/3 H_2O, C 74.67, H 12.40, N 5.12; found, C 74.55, H 12.24, N 5.39%.

5-*n*-Decyl-5-methyl-1-pyrroline *N*-oxide (1d)

This compound was prepared by a similar procedure to that used for **1a** and was obtained as a slightly yellowish oil. Yield, 29%; IR, ν 2922, 2851, 1575, 1456, 1227; ^{1}H NMR ($CDCl_3$/TMS), δ 0.88 (t, 3H), 1.27 (s, 16H), 1.42 (s, 3H), 1.6–1.9 (m, 2H), 1.97–2.3 (m, 2H), 2.4–2.7 (m, 2H), 6.98 (t, 1H); MS, *m/z* 239.2245 (calculated for $C_{15}H_{29}NO$, 239.2249), 238, 222, 140, 126, 114, 99, 98, 82, 81. Analysis: calculated for $C_{15}H_{29}NO$ + 1/4 H_2O, C 73.87, H 12.19, N 5.74; found, C 73.79, H 11.88, N 6.03%.

5-*n*-Nonyl-5-methyl-1-pyrroline *N*-oxide (1e)

This compound was prepared by a similar procedure to that used for **1a** and was obtained as a slightly yellowish oil (lit.,[11] b.p., 90–100 °C/0.005 mmHg). Yield, 60%; IR, ν 2926, 2852, 1572, 1452, 1220; ^{1}H NMR ($CDCl_3$/TMS), δ 0.88 (t, 3H), 1.27 (s, 14H), 1.41 (s, 3H), 1.6–1.9 (m, 2H), 1.95–2.3 (m, 2H), 2.4–2.7 (m, 2H), 6.86 (t, 1H, J = 2.5 Hz); MS, *m/z* 225.2087 (calculated for $C_{14}H_{27}NO$, 225.2092), 208, 126, 99, 98, 82, 81. Analysis: calculated for $C_{14}H_{27}NO$, C 74.60, H 12.08, N 6.21; found, C 74.13, H 11.99, N 6.71%.

5-*n*-Octyl-5-methyl-1-pyrroline *N*-oxide (1f)

The procedure used for the preparation of **1a** was adapted. An aqueous solution saturated with ammonium chloride (1 ml) was added to the reactive mixture of nitrone MPO and *n*-octylmagnesium bromide, diethyl ether was removed directly from the flask by distillation and the residue was dissolved in methanol (40 ml). The subsequent procedure was similar to that used for the preparation of **1a**, and nitrone **1f** was obtained as a slightly yellowish oil. Yield, 80%; IR, ν 2926, 2853, 1572, 1452, 1229; ^{1}H NMR ($CDCl_3$/TMS), δ 0.88 (t, 3H), 1.28 (s, 12H), 1.40 (s, 3H), 1.6–1.9 (m, 2H), 2.0–2.3 (m, 2H), 2.4–2.7 (m, 2H), 6.82 (t, 1H); MS, *m/z* 211.1934 (calculated for $C_{13}H_{25}NO$, 211.1936), 210, 194, 126, 114, 99, 98, 82, 81. Analysis: calculated for $C_{13}H_{25}NO$ + 1/6 H_2O, C 72.85, H 11.91, N 6.53; found, C 72.76, H 11.48, N 7.16%.

5-*n*-Hexyl-5-methyl-1-pyrroline *N*-oxide (1g)

This compound was prepared as described for **1f**, and was obtained as a slightly yellowish oil. Yield, 49%; IR, ν 2926, 2852, 1569, 1451, 1228; ^{1}H NMR ($CDCl_3$/TMS), δ 0.87 (t, 3H), 1.27 (m, 8H), 1.40 (s, 3H), 1.6–1.9 (m, 2H), 2.0–2.3 (m, 2H), 2.4–2.7 (m, 2H), 6.85 (t, 1H); MS, *m/z* 183.1626 (calculated for $C_{11}H_{21}NO$, 183.1623), 182, 156, 126, 114, 99, 98, 82, 81.

5-*n*-Pentyl-5-methyl-1-pyrroline *N*-oxide (1h)

This compound was prepared as described for **1f**, and was obtained as a slightly yellowish oil. Yield, 43%; IR, ν 2928, 2853, 1568, 1452, 1228; ^{1}H NMR ($CDCl_3$/TMS), δ 0.88 (t, 3H), 1.27 (m, 6H), 1.38 (s, 3H), 1.6–1.9 (m, 2H), 2.0–2.3 (m, 2H), 2.4–2.7 (m, 2H), 6.79 (t, 1H); MS, *m/z* 169.1468 (calculated for $C_{10}H_{19}NO$, 169.1466), 168, 152, 140, 126, 114, 99, 98, 82, 81. Analysis: calculated for $C_{10}H_{19}NO$ + 1/6 H_2O, C 69.72, H 11.31, N 8.13; found, C 69.62, H 10.97, N 8.60%.

5-*n*-Butyl-5-methyl-1-pyrroline *N*-oxide (1i)

This compound was prepared as described for **1f**, and was obtained as a slightly yellowish oil. Yield, 33%; IR, ν 2924, 2853, 1575, 1440, 1216; ^{1}H NMR ($CDCl_3$/TMS), δ 0.90 (t, 3H), 1.25 (m, 4H), 1.39 (s, 3H), 1.6–1.9 (m, 3H), 2.0–2.3 (m, 2H), 2.4–2.7 (m, 2H), 6.80 (t, 1H); MS, *m/z* 155.1313 (calculated for $C_9H_{17}NO$, 155.1310), 154, 140, 126, 114, 99, 98, 82, 81.

5-*n*-Propyl-5-methyl-1-pyrroline *N*-oxide (1j)

This compound was prepared as described for **1f**, and was obtained as a slightly yellowish oil. Yield, 13%; IR, ν 2952, 2867, 1569, 1448, 1223; ^{1}H NMR ($CDCl_3$/TMS), δ 0.93 (t, 3H), 1.24 (m, 2H), 1.38 (s, 3H), 1.6–1.9 (m, 2H), 2.0–2.3 (m, 2H), 2.4–2.7 (m, 2H), 6.83 (t, 1H); MS, *m/z* 141.1147 (calculated for $C_8H_{15}NO$, 141.1153), 126, 124, 114, 99, 98, 82, 81.

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