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NITROXIDES (AMINYL OXIDES) - XL.[1]

ESR SPECTROSCOPIC STUDIES OF ß-SULFONYL SUBSTITUTED VINYL NITROXIDES AND OF A VINYLOGOUS NITRONYL NITROXIDE[2]

Hans Günter Aurich* and Klaus-Dieter Möbus
Fachbereich Chemie, University of Marburg, Hans-Meerwein-Straße,
D-3550 Marburg, Federal Republic of Germany

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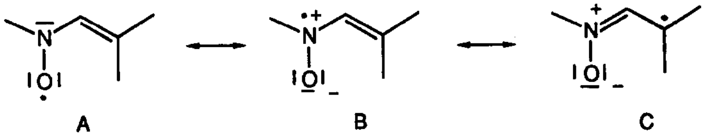
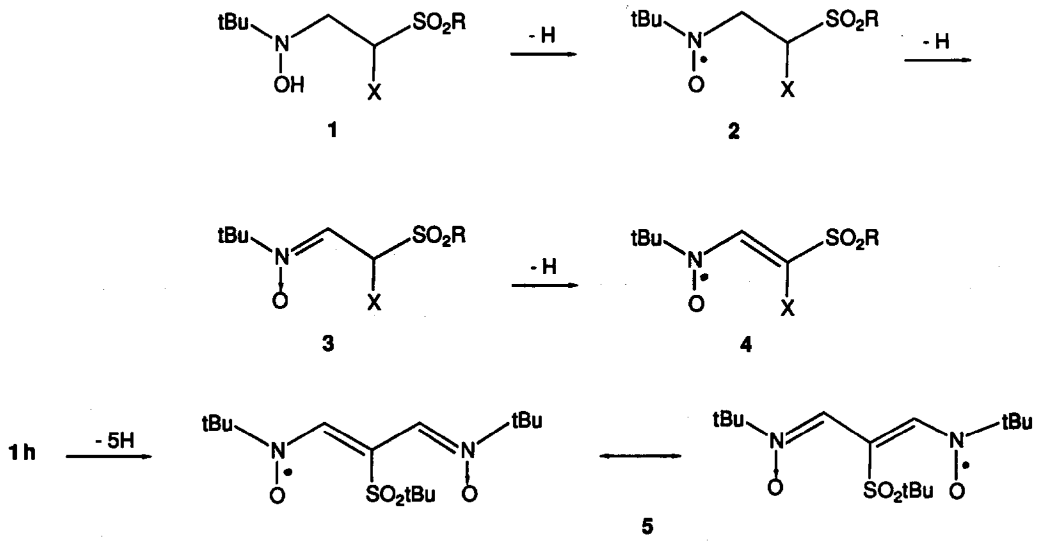
Abstract. - Oxidation of hydroxylamines **1** affords the vinyl nitroxides **4** via **2** and **3**. The vinylogous nitronyl nitroxide **5** is formed upon oxidation of **1h**. Whereas the methyl group X in **4a** is freely rotating, rotation of substituents X in **4b-d** is restricted as is indicated by their ESR spectra. Particularly, the less hindered vinyl nitroxides **4e-g** form spin adducts **6** or **7** with their precursor nitrones **3**. **4b** coexists with **6b** or **7b** between -30° and +15°C, below -30°C only **6b/7b**, above +15°C only **4b** can be detected. The two NO groups of **5** are not equivalent at room temperature and below, due to twisting of the π system. However, a dynamic process makes them equivalent at +65°C.

In vinyl nitroxides delocalization of the unpaired electron from the nitroxide group to the ß-carbon atom occurs (see formulas A-C). For this reason vinyl nitroxides are generally rather reactive radicals that can be only detected by ESR spectroscopy if they are stabilized, for instance by electron-accepting functional group at the ß-carbon atom.[1,3] To get more insight into the properties of such radicals we studied some ß-sulfonyl-substituted vinyl nitroxides and a vinylogous nitronyl nitroxide by ESR spectroscopy as well as by identification of their reaction products.[4]



Oxidation of the hydroxylamines **1** at first affords the t-butyl alkylnitroxides **2** which have ESR coupling constants typical for dialkylnitroxides[5]. (a^N = 15.25-16.00 G; $a^H_{\alpha-C}$ = 7.5 (1H)+15.5(1H) (**2a**) - 9.3-12.0 (1H)+13.3-15.85(1H) (**2b-d**) - 12.25-12.5(2H) (**2e-g**)). On further oxidation the vinyl nitroxides **4** are formed via nitrone intermediates **3**. Two additional oxidation steps occur with hydroxylamine **1h**, giving the vinylogous nitronyl nitroxide **5**. The ESR data of radicals **4** and **5** are summarized in Table 1.



	R	X		R	X		R	X
a	p-Tol	Me	**d**	t-Bu	CH_2-CH_2-CH=CH_2	**g**	allyl	H
b	t-Bu	CH_2-CH=CMe_2	**e**	Me	H	**h**	t-Bu	CH_2-N(OH)tBu
c	t-Bu	CH_2-C≡C-Ph	**f**	n-Pr	H			

Table 1. ESR coupling constants (in Gauß) of radicals **4** and **5** in chloroform solution at +20°C.

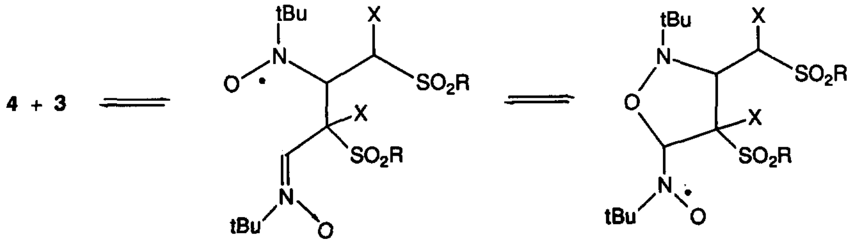
	a^N	$a^H_{\alpha\text{-C}}$	a^H_X		a^N	$a^H_{\alpha\text{-C}}$	a^H_X
4a	8.65	2.5	8.55(3H)	**4f**[c]	8.25	1.5	8.25(1H)
4b	8.25	2.65	9.7(1H);<0.3(1H)[a]	**4g**[d]	8.0	1.5	8.0(1H)
4c	7.90	2.22	9.5(1H);<0.4(1H)	**5**[e]	4.75(1N) 3.3(1N)	4.75(1H) 3.3(1H)	- -
4d	8.30	2.65	5.4(1H);1.45(1H)[b]				

[a] At +60°C broadened lines from two equivalent protons a^H = 4.9 G; [b] These two coupling constants were ascribed to the protons at the γ-C atom in accordance with the effect of line broadening. - Additional splitting of one proton a^H = 2.65 G (1H); [c] Additional splitting of R: a^H = 1.0 G (3H) - The signals are partly superimposed by the spectrum of **6f/7f**; [d] Additional splitting of R: a^H = 1.1 G (3H) - The signals are partly superimposed by the spectrum of **6g/7g**; [e] At +65°C: a^N = 4.03 G (2N); a^H = 4.03 G (2H) - see text

Using the simplified equation $a^N = 33.1\cdot\ \rho^N$ G[6] the spin density at the nitrogen atom of **4a-d**, **f** and **g** may be estimated approximately to $\rho^N = 0.24$-0.26 in good accordance with the value $\rho^N = 0.25$ for the vinyl nitroxide **4** (R = Ph, X = H)[7]. For **4a** and for **4f,g** a spin density of about 0.3 is determined for the β-C atom from the coupling constants of the methyl protons of **4a**[8] and the proton at β-C of **4f,g**[9], respectively. Thus the spin density distribution in **4a-d,f** and **g** is not only comparable to that in the related sulfonyl-substituted vinyl nitroxide **4** (R = Ph, X = H) but also to the spin density distribution in many other β-acceptor-substituted vinyl nitroxides[3]. The coupling constants $a^N = 4.75$ G and $a^N = 3.3$ G for the two nitrogen atoms of **5** correspond to a considerably reduced spin density of $\rho^N = 0.14$ and $\rho^N = 0.10$, respectively, due to the enhanced delocalization of the unpaired electron.

Whereas **4a-d** and **5** are stable in chloroform solution at room temperature for a longer period, **4f** and **g** are rather unstable. Thus the ESR signals of the latter were superimposed by the signals of either primary radicals **2** or subsequently formed radicals **6/7**. **4e** could be never observed. Obviously, the greater stability of **4a-d** must be attributed to the better steric shielding of the reactive β-position by the groups X.

In principle the vinyl nitroxides **4** can react with their precursor nitrones **3** forming spin adducts **6** or **7**.[3,10] On oxidation of **1e** only a spin adduct could be observed. Due to its relatively low nitrogen coupling constant (table 2) structure **7e** seems to be more appropriate. Radicals **7f** and **g** (or **6f** and **g**) are formed as the main products in the oxidation of hydroxylamines **1f** and **g**, along with the vinyl nitroxides **4e** and **f**. Their nitrogen coupling constants are in accordance with that of a similar radical **7** (R = Ph, X = H).[7] However, a spin adduct is formed likewise by addition of **4b** to **3b** if the temperature of the solution is lowered. Between -50°C and -30°C spin adduct **6b** or **7b** is the only radical observed, whereas between -30°C and +15°C the spin adduct coexists with the vinyl nitroxide **4b**, which is the only radical at temperatures above +15°C.[20]



6 **7**

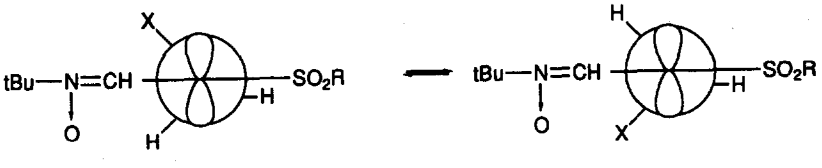
Table 2. ESR coupling constants (in Gauß) of spin adducts **6** or **7** in chloroform solution at +20°C.

	a^N	$a^H_{\alpha-C}$		a^N	$a^H_{\alpha-C}$
6/7b[a]	14.1	<0.6	**6/7f**	13.0	1.5
6/7e	12.6	<1.0	**6/7g**	13.5	1.0

[a] at -30°C

In vinyl nitroxide **4a** the methyl group X is freely rotating as is indicated by the equal couplings of the three protons. In contrast, for vinyl nitroxides **4b-d** rotation about the C-X bond is restricted. Whereas in **4d** the coupling constants of the two protons at the γ-C atom are different, in **4b** and **c** the coupling of one of these protons is so small that only splitting by the second proton is observed. Thus radicals **4b-d** must adopt a conformation which can be approximately described by Newman projections A or B.[11]

Since the ESR lines of **4b** and **c** are sharp at room temperature the interconversion of conformations A and B must be slow on the ESR time scale. The line broadening of the spectrum of **4d**, however, points to a moderate exchange of the two conformations at room temperature.[12] At 60°C six new lines appear in the spectrum of **4b** indicating that the two protons became now equivalent. The interconversion of their positions occurs at a moderate rate as is indicated by the broadening of these lines. Radicals **4c** and **d** did not survive at temperatures above 30°C.



A B

In the ESR spectrum of the vinylogous nitronyl nitroxide **5** different coupling constants for the two nitrogen atoms as well as for the two hydrogen atoms at the α C atom are found at room temperature and below, whereas at +65°C the two N atoms as well as the H atoms become equivalent (see Figure 1).

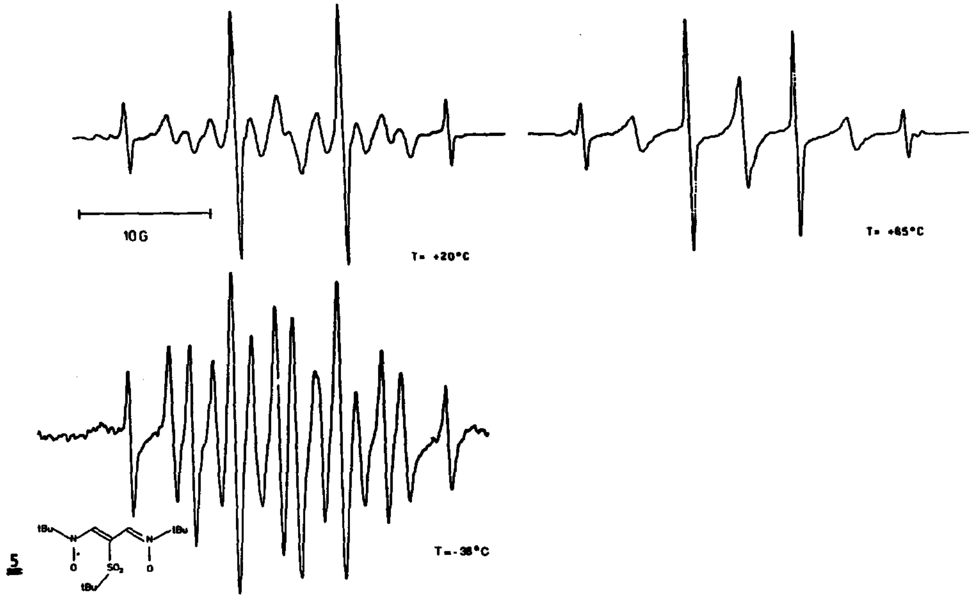


Figure 1. ESR spectrum of the vinylogous nitronyl nitroxide 5 at +65°C, +20°C and -38°C.

At +20°C most of the lines are significantly broadened, only lines 1, 5, 10 and 14 remaining sharp. This is in accordance with the correlation between nuclear spin configuration and line broadening indicating a dynamic process[12] by which the two N atoms as well as the two H atoms exchange their positions (see Table 3). At +65°C this process is fast enough to make the couplings equivalent on the ESR time scale producing a seven line spectrum in which, however, lines 2, 4,and 6 are still broadened.

Thus, the conclusion may be drawn, that a synchronous rotation about both α.C-ß.C-bonds interchanges two preferred conformations of the molecule in which the π-orbitals of one of the NO group, the adjacent α.C and ß.C-atom form one subunit of the π-system and the second NO group and the adjacent α-C atom form the other subunit. The two subunits are twisted against each other, so that delocalization from one part to the other is somewhat restricted. Presumably, the steric interaction with the tert-butyl sulfonyl group is responsible for this situation, the interchange of the two CNO subunits being coupled finally with the rotation of the tert butyl sulfonyl group around the ß-C.S bond.

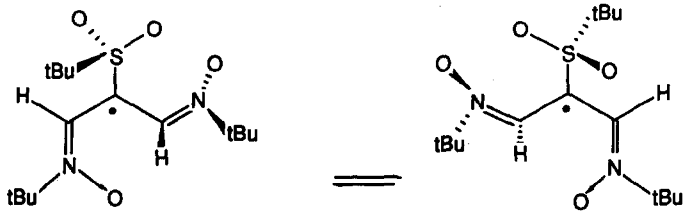
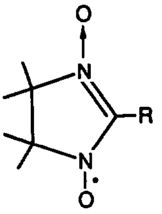


Table 3. Correlation between nuclear spin configuration and line broadening[12] caused by the dynamic process of radical **5** (given only for the low-field half of the spectrum - N_A and H_A correspond to a = 4.75 G; N_B and H_B to a = 3.3 G)

Line		Nuclear Spin State				Position of the Line (Distance from the Center in G)	Exchange with Position	Line Shift Δ (in G)
		N_A	N_B	H_A	H_B			
1		+1	+1	+1/2	+1/2	12.08	-	0
2	a	+1	+1	+1/2	-1/2	8.78	3a	-1.45
	b	+1	0	+1/2	+1/2	8.78	3b	-1.45
3	a	+1	+1	-1/2	+1/2	7.43	2a	+1.45
	b	0	+1	+1/2	+1/2	7.43	2b	+1.45
4	a	+1	0	+1/2	-1/2	5.48	6a	-2.9
	b	+1	-1	+1/2	+1/2	5.48	6b	-2.9
5	a	+1	+1	-1/2	-1/2	4.03	-	0
	b	0	+1	+1/2	-1/2	4.03	5c	0
	c	+1	0	-1/2	+1/2	4.03	5b	0
	d	0	0	+1/2	+1/2	4.03	-	0
6	a	0	+1	-1/2	+1/2	2.58	4a	+2.9
	b	-1	+1	+1/2	+1/2	2.58	4b	+2.9
6*		+1	-1	+1/2	-1/2	2.18	9*	-4.36
7	a	+1	0	-1/2	-1/2	0.72	8a	-1.45
	b	+1	-1	-1/2	+1/2	0.72	8b	-1.45
	c	0	0	+1/2	-1/2	0.72	8c	-1.45
	d	0	-1	+1/2	+1/2	0.72	8d	-1.45

* this component is not resolved

A comparison of the nitrogen coupling constants a^N of the vinylogous nitronyl nitroxide **5** with those of several types of nitronyl nitroxides (**8**-**10**) reveals a reduced spin density at nitrogen (ρ = 0.14 and 0.10 as compared to 0.20-0.23) due to the extension of the π-system, although there is some twisting in **5**. On the other hand, there is a close resemblance to the a^N value of the pyrazolyl-3-oxide-1-oxyl[16] **11** in spite of its cyclic conjugation and planarity.



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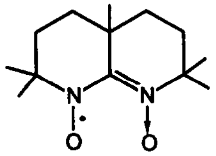
a^N :7,4-7,5G[13]



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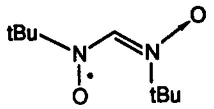
7,64G[14]



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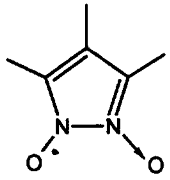
6,5G[15]



11

4,4G[16]

EXPERIMENTAL PART

The ESR measurements were performed with Varian EE9 and EE12 spectrometers. $CDCl_3$ was used as solvent for the NMR measurements. Chemical shifts are reported with reference to tetramethylsilane. ^1H-NMR spectra were obtained on Bruker AM 400 and AC 300 spectrometers. ^{13}C-NMR spectra were recorded on Bruker AM 400 and AC 300 as well as on Jeol FX 100 spectrometers. MS spectra were determined with Varian CH 7 (EI) and 711 (FD) spectrometers.

ESR Spectra of the radicals. An excess of lead dioxide was filled into an ESR tube. Subsequently, a 10^{-3} to 10^{-4} m solution of the hydroxylamine **1** in chloroform was added. After several freezing/degassing cycles the tube was sealed and shaken for a short period. Then the spectrum was recorded.

A. Vinyl sulfones

Methyl vinyl sulfone was commercially available. According to known procedures were prepared: 2-(4-tolylsulfonyl)propene[17], 2-(tert-butylsulfonyl)-5-methyl-1,4-hexadiene[18], allyl vinyl sulfone[19].

The following compounds were obtained by analogous procedures:

2-(tert-Butylsulfonyl)-5-phenyl-1-penten-4-yne as yellow oil in 42% yield[18] - MS(FD): m/e = 262 (M+,100%)- IR: ν^- = 2230 cm^{-1} (-C≡C-)- . ^1H-NMR: δ = 1.50 (s, t-Bu), 2.40 (m, 2H, H-3), 6.26 (m, 1H, H-1), 6.43 (m, 1H, H-1) 7.22-7.50 ppm (m, 5H, Ph).

2-(tert-Butylsulfonyl)-1,5-hexadiene as yellow oil in 78% yield[18]: ^1H-NMR: δ = 1.37 (s, t-Bu), 2.38 (dt, 2H, H-4), 2.58 (t, 2H, H-3), 5.07 (m, 2H, H-6), 5.81 (m, 1H, H-5), 5.97 (m, 1H, H-1), 6.22 ppm (m, 1H, H-1); J(3/4) = 6.6; (4/5) = 6.4 Hz.

Propylvinylsulfone as yellow oil in 89% yield[19]: ^1H-NMR: δ = 0.80 (t, 3H, CH_3), 1.06 (m, 2H, $C\underline{H}_2$-CH_3), 2.73 (m, 2H, SO_2-CH_2-), 5.93 (d, 1H, $C\underline{H}_2$=CH), 6.12 (d, 1H, $C\underline{H}_2$=CH), 6.44 ppm (dd, CH_2=C$\underline{H}$); J(CH_2-CH_3) = 7.4; (CH_2=CH) = 16.6 and 10.0 Hz); ^{13}C-NMR: δ = 12.7 (q, CH_3), 15.9 (t, $\underline{C}H_2$-CH_3), 55.4 (t, SO_2-CH_2-), 129.9 (t, CH_2=), 136.2 (d, CH=).

B. Addition of t-butylhydroxylamine to vinyl sulfones

A solution of 22 mmol N-tert-butylhydroxylamine in dichloromethane was added to a solution of 20 mmol vinyl sulfone in the same solvent at 0°C. The solution was then stirred at room temperature for 1 to 5 days. After removal of the solvent residual starting material was removed under vacuum. In most cases crystallization occurred on treatment with diethyl ether.

1-(N-tert-Butylhydroxyamino)-2-(4-tolylsulfonyl)propane (**1a**): Colourless oil in 54% yield. ^{1}H-NMR: δ = 1.03 (s, tBu), 1.33 (d, 3H, H-3), 2.43 (s, 3H, CH_3-tolyl), 2.60-3.53 (m, 3H, H-1 and H-2), 5.57 (s, broad, 1H, OH), 7.02-7.80 ppm (m, 4H, tolyl); J(2/3) = 7.0 Hz.

6-(N-tert-Butylhydroxyamino)-5-(tert-butylsulfonyl)-2-methyl-2-hexene (**1b**): Colourless solid, m.p. 75-76°C from diethyl ether/hexane. $C_{15}H_{31}NO_3S$ (305.4) Calcd. C 59.00 H 10.23 N 4.59 Found C 58.31 H 10.25 N 4.50; MS(EI): m/e = 305 (M^+, 4.5%); ^{1}H-NMR: δ = 1.09 (s, t-Bu-N), 1.43 (s, tBu-S), 1.66 (s, CH_3), 1.71 (s, CH_3), 2.60 (m, H-4), 2.71 (m, H-4′), 2.90 (dd, H-6), 3.12 (dd, H-6′), 3.56 (m, H-5), 4.38 (s broad, 1H, OH), 5.31 ppm (t, H-3); J(3/4) = 7.0, (3/4′) = 7.0, (5/6) = 8.8, (5/6′) = 3.8, (6/6′) = 13.6 Hz; ^{13}C-NMR: δ = 17.7 (t, C-4), 23.5 (q, t-Bu-S), 24.9 (q, t-Bu-N), 25.5 (q, CH_3), 26.6 (q, CH_3), 51.1 (t, C-6), 55.8 (d, C-5), 58.7 (s, t-Bu-N), 60.7 (s, t-Bu-S), 120.4 (d, C-3), 133.6 ppm (s, C-2).

5-(N-tert-Butylhydroxyamino)-4-(tert-butylsulfonyl)-1-phenyl-1-pentyne (**1c**): colourless solid in 72% yield, m.p. 139-140°C from diethyl ether. $C_{19}H_{29}NO_3S$ (351.4) Calcd. C 64.94 H 8.32 N 3.99 Found C 64.77 H 8.29 N 3.49. MS(FD): m/e = 351 (M^+, 100%). ^{1}H-NMR: δ = 1.14 (s, t-Bu-N), 1.48 (s, t-Bu-S), 3.10 (m, 2H, H-3 or H-5), 3.16 (m, 2H, H-5 or H-3), 3.79 (m, H-4), 4.60 (s broad, 1H, OH), 7.26-7.40 ppm (m, 5H, Ph); ^{13}C-NMR: δ = 18.6 (t, C-3), 23.6 (q, tBu-S), 25.2 (q, tBu-N), 51.2 (t, C-5), 54.9 (d, C-4), 59.1 (s, tBu-N), 61.1 (s, tBu-S), 82.5 (s, C-2), 89.5 (s, C-1), 123.9 (s, Ph), 127.8, 128.1 and 131.5 ppm (d, Ph).

6-(N-tert-Butylhydroxyamino)-5-(tert-butylsulfonyl)-1-hexene (**1d**) was only formed to a minor amount and could not be separated from other components. The following data confirm the formation of **1d**: MS(EI): m/e = 289 (M^+, 2.3%). ^{13}C-NMR: δ = 13.8 (t, C-4), 23.3/23.4 (q, tBu-S), 24.8/25.0 (q, tBu-N), 31.3/32.1 (t, C-3), 51.9/52.8 (t, C-6), 53.1/54.7 (d, C-5), 58.1/58.7 (s, t-Bu-N), 60.2/60.6 (s, t-Bu-S), 114.9 (t, C-1), 137.6 ppm (d, C-2).

2-(N-tert-Butylhydroxyamino)-1-(methylsulfonyl)ethane (**1e**): colourless solid in 54% yield, m.p. 30-32°C. ^{1}H-NMR: δ = 1.06 (s, t-Bu), 2.93 (s, CH_3), 3.07 (t, 2H, H-1), 3.26 (t, 2H, H-2), 6.42 ppm (s, broad, 1H, OH). J(1/2) = 6.0 Hz. ^{13}C-NMR: δ = 24.8 (q, t-Bu), 42.3 (q, CH_3), 46.1 (t, C-2), 53.5 (t, C-1), 59.2 ppm (s, t-Bu).

2-(N-tert-Butylhydroxyamino)-1-(propylsulfonyl)ethane (**1f**): colourless crystals in 98% yield, m.p. 46-48°C from ether. $C_9H_{21}NO_3S$ (223.2) Calcd. C 48.43 H 9.48 N 6.27 Found C 47.95 H 9.17 N 6.29. MS(EI): m/e = 223 (M^+, 9%) ^{1}H-NMR: δ = 0.99 (t, CH_3), 1.05 (s, t-Bu), 1.81 (m, 2H, $C\underline{H}_2$-CH_3), 3.01 (m, 4H, $CH_2SO_2CH_2$), 3.20 (t, 2H, H-2), 5.42 ppm (s, broad, 1H, OH); J(1/2 = 6.2, (CH_3/CH_2) = 7.5 Hz. ^{13}C-NMR: δ = 13.2 (q, CH_3), 15.6 (t, $\underline{C}H_2$-CH_3), 25.1 (q, t-Bu), 45.9 (t, $-SO_2-\underline{C}H_2-CH_2-CH_3$), 51.9 (t, C-1), 55.8 (t, C-2), 59.1 ppm (s, tBu).

1-(Allylsulfonyl)-2-(N-tert-butylhydroxyamino)ethane (**1g**): yellow oil in 94% yield. MS(FD): m/e = 221 (M^+, 100%). ^{1}H-NMR: δ = 1.13 (s, t-Bu), 3.13 (t, 2H, H-1), 3.25 (t, 2H, H-2), 3.84 (d, 2H, $-C\underline{H}_2-CH=CH_2$), 5.47 (m, 2H, $-CH=C\underline{H}_2$), 5.97 ppm (m, 1H, $-C\underline{H}=CH_2$). J(1/2) = 6.1, ($-CH_2-CH=$) = 7.3 Hz. ^{13}C-NMR: δ = 24.8 (q, t-Bu), 45.5 (t, CH_2-N), 50.4 (t, CH_2SO_2), 58.6 (s, t-Bu), 58.7 (t, $\underline{C}H_2-CH=CH_2$), 124.2 (t, $\underline{C}H_2=CH$), 124.6 (d, $CH_2=\underline{C}H$).

1.3-Bis(N-tert-butylhydroxyamino)-2-(tert-butylsulfonyl)propane (**1h**): A solution of 10 mmol of 1.3-dibromo-2-(tert-butylsulfonyl)propane[18] and 50 mmol of N-tert-butylhydroxylamine in 150 ml dichloromethane was kept at room temperature for 1 week. After removal of the solvent and the excess of tert-butylhydroxylamine, **1h** crystallized from diethyl ether as a colourless solid of m.p. 136°C in 45% yield. $C_{15}H_{34}N_2O_4S$ (338.2) Calcd. C 53.22 H 10.13 N 8.28 Found C 52.05 H 9.98 N 8.06. MS(FD): m/e = 338 (M^+, 95%). ^{1}H-NMR: δ = 1.15 (s, 18H, t-Bu-N), 1.47 (s, 9H, t-Bu-S), 3.14 (m, 2H, H-1 + H-3), 3.32 (m, 2H, H-1 + H-3), 3.86 ppm (m, H-2). ^{13}C-NMR: δ = 23.5 (q, t-Bu-S), 24.8 (q, t-Bu-N), 51.3 (d, C-2), 52.7 (t, C-1 + C-3), 58.4 (s, t-Bu-N), 62.6 ppm (s, t-Bu-S).

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