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NITROXIDES (AMINYL OXIDES) - XLI.[1] FORMATION AND DIMERIZATION OF ß-SULFONYL SUBSTITUTED VINYL NITROXIDES. CC-VERSUS OC-DIMERIZATION[2]

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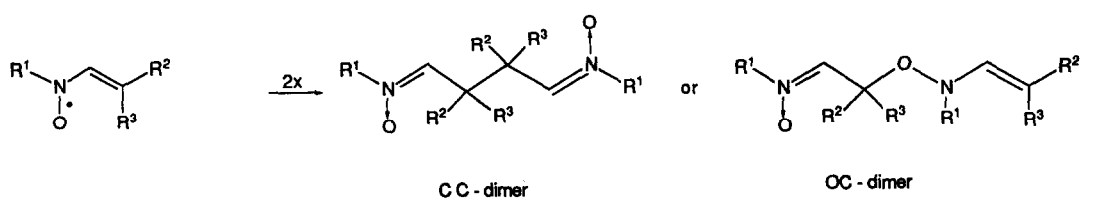
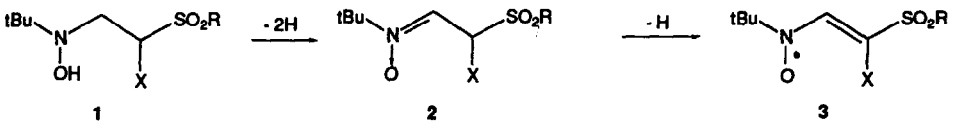
Abstract: Upon oxidation of hydroxylamines **1a-c** only nitrones **2a-c** could be isolated although the nitroxides **3a-c** were detected by ESR. Oxidation of **1f** yields compound **5**, the CC-dimer of **4**. Whereas oxidation of **1d** affords only **7d** which arises from **3d** by CC-dimerization and elimination of propylsulfinic acid, from vinyl nitroxide **3e** products **7e**, **8** and **9** are formed by CC-dimerization and subsequent reaction steps, as well as **11** which is formed via the intermediate OC-dimer **10**. The reaction steps leading to the different products are discussed.

The reactivity of vinyl nitroxides can be attributed to their tendency to undergo bond formation at the ß-C-atom. Thus, in principle they can form CC-bonded dimers or OC-bonded dimers.[3] For N-tert-butyl substituted vinyl nitroxides CC-dimerization was found to be the preferred reaction pathway at room temperature. It has been assumed that OC-dimers can be formed in a reversible reaction. However, if there is no possibility to form a more stable product in a subsequent reaction step, OC-dimerization should be only an unproductive reaction pathway.[4] To verify this assumption we have now studied the dimerization of some ß-sulfonyl substituted vinyl nitroxides **3** generated by oxidation of the corresponding hydroxylamines **1**.[1]

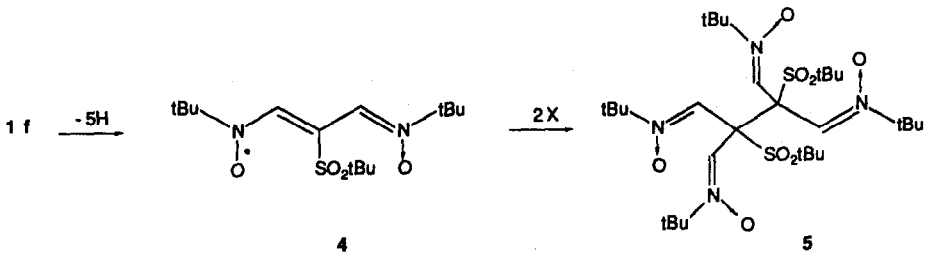


Oxidation of hydroxylamines **1** in dichloromethane exhibits significant differences. Although the vinyl nitroxides **3a-c** could be detected by ESR spectroscopy, only the nitrones **2a-c** were isolated in moderate to good yields from oxidation of hydroxylamines **1a-c** on a preparative scale. In contrast, the vinylogous nitronyl nitroxide **4** formed by oxidation of **1f** afforded the CC-dimer **5** in 61% yield.



1 2 3

	R	X		R	X		R	X
a	p-tolyl	Me	c	tBu	CH_2-C≡C-Ph	e	allyl	H
b	tBu	CH_2-CH=CMe_2	d	n-Pr	H	f	tBu	CH_2-N(OH)tBu



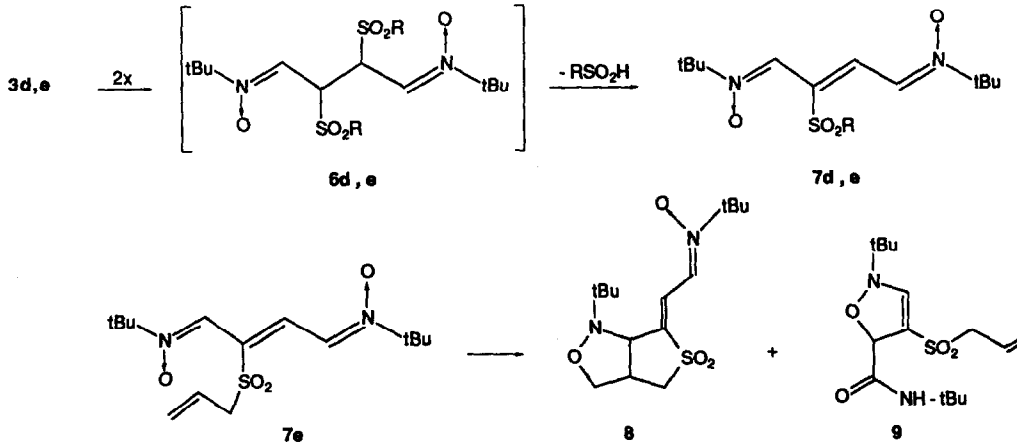
4 5

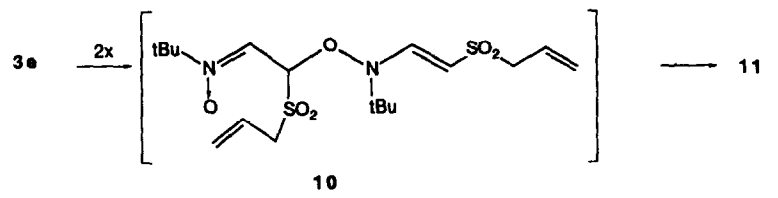
There are two factors which may be responsible for these unexpected results: 1. Oxidation of nitrones is favored by parallel orientation of the π-electrons of the nitrone group and the hydrogen at the ß-carbon atom. Since for steric reasons **2a-c** should prefer a conformation in which this hydrogen is approximately perpendicular orientated to the π-electrons, oxidation should be more difficult for such ß-disubstituted nitrones compared to the ß-monosubstituted nitrones.[5] In oxidation of **1f**, however, two nitrone groups adjacent to the ß-carbon atom can be formed. This is expected to facilitate the dehydrogenation.

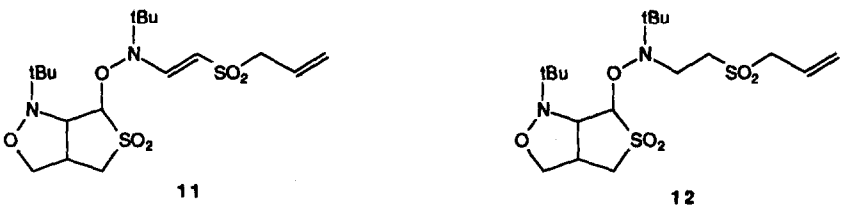
2. CC-Dimers of ß-disubstituted vinyl nitroxides are hexa-substituted ethanes, which are more or less destabilized by the steric interaction of their substituents.[6] On the other hand, the sterically less hindered OC-dimers seem to be energetically less favorable.[4] Since, furthermore, no conversion to give more stabilized products is possible, dimerization of **3a-c** is blocked. The steric destabilization of dimer **5**, however, seems to be less unfavorable since the nitrone group is more flat as compared to substituents X of vinyl nitroxides **3a-c**.

In contrast to the ß-disubstituted vinyl nitroxides CC-dimerization of **3d** and **e** to give **6d** and **e** is not affected by such disadvantages. Moreover, an additional product stabilization occurs by elimination of sulfinic acid affording conjugated dinitrones **7**. Thus, dinitrone **7d** could be isolated in 65% yield. As the NMR spectra reveal, **7d** exists in two isomeric forms. Since N-tert-butyl nitrones exist in the Z-configuration[7] it must be assumed that the two isomers differ by the configuration at their central double bond.[8]

From oxidation of **1e** at room temperature the products **7e**, **8**, **9** and **11**, formed by dimerization of vinyl nitroxide **3e**, followed by additional reaction steps, were isolated. In addition, a small amount of a bicyclic compound **12** was obtained. In refluxing chloroform the dinitrone **7e** was completely converted to products **8** and **9**. However, if the oxidation of **1e** was performed at -20°C, compound **11** and nitrone **2e**, the precursor of vinyl nitroxide **3e**, were the main products (see Table 1). Finally, using p-benzoquinone as oxidizing reagent,[9] the reaction could be totally stopped at the oxidation level of nitrone **2e**, affording a 2:1 complex of **2e** and hydroquinone.



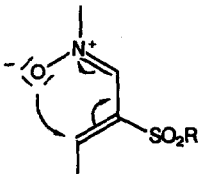


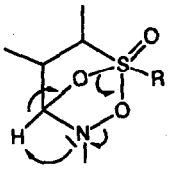


The variety of reactions products formed from **3e** is due to the various reaction pathways that arise by the introduction of the allyl moiety, in particular by the possibility of intramolecular cycloadditions between the nitrone group and the allyl group.[10,11] Thus, **8** is formed by such a cyclo-

addition from **7e**. Independently, **7e** isolated from the reaction mixture was converted to **8** on standing at room temperature.

The formation of **9** occurs on an even more complex way. The α,β-unsaturated nitrone group in **7e** can undergo a 1.5-dipolar cyclization[12] with formation of an isoxazoline ring.[8] The conversion of the nitrone group into an amide group takes place possibly by an oxygen exchange with the sulfone group via a bicyclic intermediate.[13] The order of the reaction steps is of course uncertain.





The main feature of the vinyl nitroxide **3e** is, however, the formation of compound **11**, which arises by OC-dimerization affording compound **10** as non isolable intermediate, that subsequently undergoes intramolecular cycloaddition. In other words, the usually unstable OC-dimer is trapped by itself in this specific case, because its intramolecular cycloaddition gives a more stable product. In a similar way compound **12** must arise by OC-coupling between the alkyl tert-butyl nitroxide formed in the first oxidation step of **1e** and the vinyl nitroxide **3e**.

Table 1. Products formed upon oxidation of **1e** by dimerization of vinyl nitroxide **3e** and subsequent reactions at various temperatures.

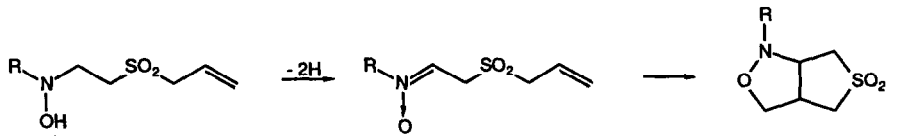
Reaction Temperature	Yields of Compounds (%) **11**	**8**	**9**	**7e**
-20°C[a]	32	trace	-	-
+23°C[b]	34	13	4	10[c]
+61°C[d]	22	16	10	-

[a] in addition 40% of nitrone **2e** were isolated; [b] in addition **12** was isolated in 3% yield; [c] **7e** underwent cycloaddition forming **8** on standing at room temperature or on heating; [d] a larger amount of decomposition products was formed at this temperature.

From the temperature dependence of the product distribution the conclusion may be drawn, that OC-dimerization is the kinetically preferred reaction pathway of this type of vinyl nitroxides. However, the OC-dimers are usually too unstable to be isolated. Thus, their formation is only an unproductive reaction pathway, if they cannot undergo a secondary reaction leading to a stable product as for instance **11**. Otherwise CC-bonded dimers, such as **6**, and

secondary reaction products which can arise from those, are formed in a thermodynamically controlled reaction.

A comparison of the behaviour of nitrones **2e** and **10** is of particular interest. Both nitrones are substituted by an allyl sulfonyl group at the ß.C-atom. However, the intramolecular cycloaddition of **2e** to afford **15e** is so slow that is is finished only after a few days at room temperature. Thus, under usual conditions it cannot compete with oxidation furnishing the products derived from vinyl nitroxide **3e**. In contrast, nitrone **10** could never be isolated, since its intramolecular cycloaddition to give **11** is very fast. The reason for this considerable enhancement by the N.N-disubstituted aminoxy group of **10e** may be an usual "Thorpe-Ingold" effect,[14] as well as a specific effect caused by the oxygen substituent at the ß-carbon atom.



1e,13g **2e,14g** **15e,g**

e: R = t-Bu g: R = 4-t-BuPh

If, however, the N-tert-butyl substituent of **2e** is replaced by an aryl group the situation is quite different. Thus, upon oxidation of **13g** only bicyclic compound **15g** could be isolated, indicating that the intramolecular cycloaddition of nitrone **14g** is now extremely fast. For this reason neither the corresponding vinyl nitroxide could be detected nor any product arising from this vinyl nitroxide was isolated. This striking differences in the behaviour of the nitrones **2e** and **14g** underline the influence of the N-substituent on the reactivity of nitrones.[4,15]

Summary. Whereas the vinylogous nitronyl nitroxide **4** affords the CC-dimer **5**, the ß-disubstituted vinyl nitroxides **3a-c** do not form isolable dimers because of the steric and electronic destabilization of such highly substituted compounds. Furthermore, formation of radicals **3a-c** by dehydrogenation of nitrones **2a-c** is restricted by an unfavorable conformational situation. In contrast, formation and dimerization of **3d** and **e** occurs without difficulties. The CC-dimerization of **3d** and **e** is additionally favored by subsequent elimination of the corresponding sulfinic acid. In particular, the possibility of intramolecular cycloaddition reactions for the dimers of **3e** opens new reaction pathways to give energetically favorable products. Thus, in addition to **7e, 8** and **9** formed by CC-dimerization and secondary reactions, bicyclic compound **11** is formed via the intermediate **10**. From the temperature dependence of the product distribution it is deduced that OC-dimerization can be the kinetically preferred reaction pathway of such vinyl nitroxides.

This is, however, only realized if a more stable compound such as **11** is formed in a subsequent reaction step. Otherwise, OC-dimerization is an unproductive reaction path, dimerization being thermodynamically controlled. Thus, more stable compounds arising by CC-dimerization and subsequent reaction steps are usually formed.

EXPERIMENTAL PART

The oxidation of the hydroxylamines **1**: A solution of hydroxylamine[1] (10 mmol) in 50 ml dichloromethane was added at 0°C to a vigorously stirred suspension of 10 g lead dioxide in dichloromethane (250 ml CH_2Cl_2 for **1a-c,f**, 100 ml for **1d** and **e**). Subsequently the reaction mixture was stirred at room temperature for several h. After separation from the lead salts the solvent was removed. With the exception of **2a** crystallization occurred when the residue was treated with diethyl ether and stored at -30°C.

N-tert-Butyl-[2-(4-tolylsulfonyl)propylidene]amine-N-oxide **(2a)** was obtained as a yellow oil in 58% yield. Reaction time: 24 h. MS(FD): m/e = 283 (M^+, 100%). ^{1}H-NMR ($CDCl_3$): δ = 1.22 (s, t-Bu), 1.48 (d, 3H, H-3), 2.35 (s, 3H, CH_3-tolyl), 4.88 (m, H-2), 6.74 (d, H-1), 7.25 (m, 2H, tolyl), 7.71 ppm (m, 2H, tolyl). J (1/2) = 8.2, (2/3) = 7.0 Hz. ^{13}C-NMR ($CDCl_3$): δ = 10.3 (q, C-3), 21.1 (q, CH_3-tolyl), 27.8 (q, t-Bu), 56.6 (d, C-2), 70.5 (s, t-Bu), 126.3 (d, J = 174 Hz, C-1); 128.1 (d), 129.2 (d), 135.3 (s) and 144.6 ppm (s) for the tolyl group.

N-tert-Butyl-[2-(tert-butylsulfonyl)-5-methyl-4-hexen-1-ylidene]amine-N-oxide **(2b)**: Reaction time 48 h. Light-yellow crystals, 86% yield, m.p. 108-109°C from diethyl ether. $C_{15}H_{29}NO_3S$ (303.4) Calcd. C 59.39 H 9.64 N 4.62 Found C 58.82 H 9.54 N 4.53. MS(EI): m/e = 303 (M^+, 6%). ^{1}H-NMR ($CDCl_3$): δ = 1.40 (s, t-Bu-S), 1.45 (s, t-Bu-N), 1.65 (s, CH_3), 1.68 (s, CH_3), 2.66 (m, H-3), 2.83 (m, H-3'), 4.93 (ddd, H-2), 5.06 (m, H-4), 6.85 ppm (d, H-1); J (1/2) = 8.5, (2/3) = 9.5, (2/3') = 5.0, (3/3') = 14.5, (3/4), 8.5 (3'/4) = 7.5 Hz. ^{13}C-NMR ($CDCl_3$): δ = 17.7 (t, C-3), 22.7 (q, t-Bu-S), 25.4 (q, CH_3), 25.6 (q, CH_3), 27.4 (q, t-Bu-N), 52.9 (d, C-2), 60.8 (s, t-Bu-S), 70.3 (s, t-Bu-N), 117.3 (d, C-4), 128.6 (d, J = 182 Hz, C-1), 135.6 ppm (s, C-5).

N-tert-Butyl-[2-(tert-butylsulfonyl)-5-phenyl-4-pentyn-1-ylidene]amine-N-oxide **(2c)**: Reaction time 24 h, light-brown crystals, 64% yield, m.p. 69°C from diethyl ether $C_{19}H_{27}NO_3S$ (349.4) Calcd. C 65.32 H 7.79 N 4.01 Found C 64.77 H 7.76 N 3.99. ^{1}H-NMR ($CDCl_3$): δ = 1.37 (s, t-Bu-S), 1.41 (s, t-Bu-N), 3.03 (dd, H-3), 3.17 (dd, H-3'), 5.14 (ddd, H-2), 7.01 (d, H-1), 7.19-7.30 ppm (m, 5H, Ph). J (1/2 = 8.4, (2/3) = 10.0, (2/3') = 5.0, (3/3') = 17.0 Hz. ^{13}C-NMR ($CDCl_3$): δ = 18.6 (t, C-3), 23.0 (q, t-Bu-S), 27.9 (q, t-Bu-N), 52.5 (d, C-2), 61.6 (s, t-Bu-S), 71.2 (s, t-Bu-N), 83.1 (s, C-4), 84.1 (s, C-5); - 123.3 (s), 127.8 (d), 128.5 (d), 128.6 (d) phenyl-131.9 ppm (d, J = 169 Hz, C-1).

Oxidation of **1f** for 36 h afforded the CC-dimer of nitroxide **4**, the compound **5**, in 61% yield as yellow solid, m.p. 112-113°C from diethyl ether. $C_{30}H_{58}N_4O_8S_2$ (666.7) Calcd. C 54.04 H 8.77 N 8.40 Found C 53.84 H 8.77 N 8.40. ^{1}H-NMR ($CDCl_3$): δ = 1.33 (s, 18H, t-Bu-S); 1.45 (s, 36H, t-Bu-N), 7.45 ppm (s, 4H, CH=N). ^{13}C-NMR ($CDCl_3$): δ = 23.9 (q, t-Bu-S), 27.5 (q, t-Bu-N), 61.6 (s, t-Bu-S), 65.7 (s, t-Bu-N), 102.5 (s, central C), 139.5 (d, J = 175 Hz, -CH=N).

N,N'-[2-(Propylsulfonyl)-2-butene-1,4-diylidene]bis(tert-butylamine-N-oxide) (**7d**): Reaction time 5 h, orange crystals, 65% yield, m.p. 111°C from diethyl ether. $C_{15}H_{28}N_2O_4S$ (332.4) Calcd. C 54.21 H 8.49 N 8.43 Found C 53.96 H 8.40 N 8.64. **7d** exists in two stereoisomeric forms, presumably the ZEZ and ZZZ forms, in an approximate ratio of 1:1, as the NMR spectra reveal. ^{1}H-NMR ($CDCl_3$): δ = 0.93/0.98 (t, 3H, CH_3), 1.46/1.47/1.47/1.51 (s, 18H, t-Bu), 1.70 (m, 2H, CH_2-CH_3), 2.91 (m, 2H, SO_2-CH_2-), 7.60/7.68 (s, H-1/1'), 7.69/8.56 (d, H-3/3'), 7.79/9.83 ppm (d, H-4/4'). J (3/4) = 9.9, (3'/4') = 10.8 Hz. ^{13}C-NMR ($CDCl_3$): δ = 13.0 (2q, CH_3), 16.3 (2t, CH_2-CH_3), 28.1-28.3 (4q, t-Bu), 57.5/58.3 (t, CH_2-SO_2), 72.2/72.3/72.8/73.0 (s, t-Bu), 123.2/123.9 (d, J = 184 and 181 Hz, C-4), 125.2/129.2 (d, J = 168 and 166 Hz, C-3), 128.4/130.4 (d, J = 184 and 187 Hz, C-1), 131.0/131.9 ppm (s, C-2).

Products from oxidation of **1e**: Reaction time 5 h at room temperature. After removal of lead salts and solvent the residue was treated with diethyl ether. The remaining solid was recrystallized from ethanol giving white crystals of compound **11** in 34% yield, m.p. 148°C. $C_{18}H_{32}N_2O_6S_2$ (436.4) Calcd. C 49.54 H 7.39 N 6.42 Found C 49.06 H 7.28 N 6.33. MS(FD): m/e = 436 (M^+, 100%). ^{1}H-NMR ($CDCl_3$): δ = 1.17 (s, t-Bu), 1.37 (s, t-Bu), 3.02 (dd, H-6'), 3.33 (ddddd, H-5), 3.44 (dd, H-6), 3.66 (dd, H-4'), 3.75 (d, 2H, -CH_2-CH=), 4.01 (t, H-1), 4.26 (dd, H-4), 4.86 ppm (broadened, H-8),5.43 (m, 2H, CH=CH_2), 5.96 (m, 1H, CH=CH_2), 6.48 (m, broad, 1H, =CH-SO_2), 7.26 (d, 1H, N-CH=). J (1/5) = 9.0, (1/8) = 9.0, (4/4') = 8.8, (4/5) = 8.2, (4'/5) = 4.4, (5/6) = 9.4), (5/6') = 7.7, (6/6') = 13.6 Hz. ^{13}C-NMR ($CDCl_3$): δ = 26.7 (q, t-Bu), 27.1 (q, t-Bu), 38.9 (d, C-5), 51.0 (t, C-6), 60.3 (s, t-Bu), 60.6 (t, CH_2-SO_2), 62.1 (d, C-1), 64.5 (s, t-Bu), 74.4 (t, C-4), 95.6 (d, C-8), 106.5 (d, =CH-SO_2), 124.2 (t, C=CH_2), 125.4 (d, -CH=CH_2), 146.4 ppm (d, =CH-N).

Subsequently, the ether solution was concentrated and stored at -30°C until crystallization occurred. **8** was obtained in 13% yield. Yellow crystals of m.p. 109°C. $C_{15}H_{26}N_2O_4S$ (330.4) Calcd. C 54.54 H 7.93 N 8.48 Found C 53.85 H 7.93 N 8.27. MS (FD): m/e = 330 (M^+, 100%). ^{1}H-NMR ($CDCl_3$): δ = 1.23 (s, t-Bu), 1.54 (s, t-Bu), 3.00 (dd, H-6'), 3.42 (ddddd, H-5), 3.49 (dd, H-6), 3.62 (dd, H-4'), 4.36 (t, H-4), 4.72 (dd, H-1), 7.69 (dd, =CH-CH=N-), 8.63 ppm (d, -CH=N). J (1/5) = 8.1, ^{4}J (1/=CH) = 2.5, J (4/4') = 8.2, (4/5) = 8.2, (4'/5) = 6.2, (5/6) = 8.9, (5/6') = 3.4, (6/6') = 13.0, (=CH-CH=) = 9.7 Hz; ^{13}C-NMR

($CDCl_3$): δ = 27.1 (q, t-Bu), 28.2 (q, t-Bu), 41.3 (d, C-5), 52.4 (t, C-6), 60.6 (s, t-Bu), 61.5 (d, C-1), 71.8 (s, t-Bu), 74.0 (t, C-4), 124.0 (d, J = 162 Hz, =CH-CH=), 125.7 (d, J = 180 Hz, -CH=N), 141.6 ppm (s, C-8).

After several days a small amount of compound **12** was crystallized from the ether solution. Yellow crystals, m.p. 148°C, 3% yield. $C_{18}H_{34}N_2O_6S$ (438.4) Calcd. C 49.31 H 7.82 N 6.39 Found C 49.23 H 7.47 N 6.33. MS(FD): m/e = 438 (M^+, 100%). ^{1}H-NMR ($CDCl_3$): δ = 1.14 (s, t-Bu), 1.22 (s, t-Bu), 3.02 (dd, H-6'), 3.23 (ddddd, H-5), 3.38 (dd, H-6), 3.50 (m, 2H, N-CH_2), 3.64 (dd, H-4'), 3.76 (m, 4H, CH_2-SO_2-CH_2), 3.86 (t, H-1), 4.22 (dd, H-4), 4.92 ppm (d, H-8), 5.47 (m, 2H, CH=CH_2), 5.96 (m, 1H, CH=CH_2). J (1/5) = 8.6, (1/8) = 8.6, (4/4') = 8.7, (4/5) = 7.9, (4'/5) = 5.0, (5/6) = 9.3, (5/6') = 7.9, (6/6') = 13.9 Hz. ^{13}C-NMR ($CDCl_3$): δ = 25.4 (q, t-Bu), 26.9 (q, t-Bu), 38.7 (d, C-5), 46.9 (t, CH_2-N), 50.8 (t, CH_2SO_2), 51.1 (t, C-6), 58.3 (s, tBu), 60.0 (s, t-Bu), 62.3 (t, -CH_2-CH=), 62.6 (d, C-1), 73.9 (d, C-4), 97.3 (d, C-8), 124.2 (d, -CH=CH_2), 124.8 ppm (t, CH=CH_2).

The residue obtained by evaporation of the ether was dissolved in ethyl acetate. Thin-layer chromatography on silica gel gave two main fractions.

Compound **9**: R_f = 0.78, yellow solid in 4% yield, m.p. 135°C. $C_{15}H_{26}NO_4S$ (330.4) Calcd. C 54.54 H 7.93 N 8.48 Found C 53.37 H 7.92 N 8.21. ^{1}H-NMR ($CDCl_3$): δ = 1.13 (s, t-Bu), 1.42 (s, t-Bu), 2.52 (s, broad, exchangeable with D_2O, NH), 3.04 (d, 2H, CH_2-CH=), 5.01 (s, broad, sharpened after H-D exchange, H-5), 5.27 (m, 2H, -CH=CH_2), 5.72 (m, -CH=CH_2), 7.98 ppm (s, H-3). ^{13}C-NMR ($CDCl_3$): δ = 27.5 (q, t-Bu), 30.1 (q, t-Bu), 50.5 (s, t-Bu), 58.7 (t, CH_2-CH=), 63.9 (s, t-Bu), 89.1 (d, C-5), 99.9 (s, C-4), 123.7 (t, CH=CH_2), 125.9 (d, CH=CH_2), 142.4 (d, J = 178 Hz, C-3), 177.2 ppm (s, C=O).

N,N'-[2-(Allylsulfonyl)-2-butene-1,4-diylidene]bis(tert-butylamine-N-oxide (**7e**): R_f = 0.70, yellow oil in 10% yield. MS (FD): m/e = 330 (M^+, 100%). **7e** exists in two stereoisomeric forms (presumably ZEZ and ZZZ) as the NMR spectra reveal. ^{1}H-NMR ($CDCl_3$): δ = 1.46/1.47/1.48/1.49 (s, t-Bu), 3.67/3.69 (d, 2H, SO_2-CH_2), 5.23-5.46 (m, 2H, CH=CH_2), 5.67-5.78 (m, H, CH=CH_2), 7.55/7.61 (s, H-1/1'), 7.65/8.54 (d, H-3/3'), 7.74/9.84 ppm (d, H-4/4'). J (3/4) = 9.9, J (3'/4') = 10.8 Hz. ^{13}C-NMR ($CDCl_3$): δ = 28.1-28.2 (4q, t-Bu), 60.8/61.4 (t, CH_2-CH=), 72.2/72.6/72.9/73.9 (s,t-Bu), 123.7-130.3 ppm (2t, 8d, 2s). On heating as well as on standing at room temperature **7e** underwent conversion affording **8**.

The oxidation of **1e** at -20°C was performed for 3 days. **11** was isolated in the same way as described before in 32% yield. From the filtrate the solvent was removed. A sample of the residue was dissolved in deuteriochloroform. As the NMR spectrum revealed it consisted mainly of nitrone **2e** with a small impurity of bicyclic compound **8**. The main part of this substance was completley converted into the bicyclic compound **15e** after refluxing in chlo-

roform solution for four h. The oxidation at +61°C was performed in boiling chloroform for five h. Products were isolated by the same procedure as described before.

2:1-complex of N-[2-(allylsulfonyl)ethylidene]-tert-butylamine-N-oxide (**2e**) and hydroquinone: Oxidation of the hydroxylamine **1e** with p-benzoquinone in benzene according to the procedure of Fujita and Sano[9] gave 47% yield. M.p. 83-84°C from diethyl ether. - $C_{24}H_{40}N_2O_8S_2$ (548.5) Calcd. C 52.53 H 7.35 N 5.11 Found C 52.11 H 7.39 N 5.01 - ^{1}H-NMR: δ = 1.53 (s, t-Bu), 3.77 (d, 2H, -C$\underline{H}_2$-CH=CH_2), 4.21 (d, 2H, H-2), 5.54 (m, 2H, CH=C$\underline{H}_2$), 5.96(m, 1H, C$\underline{H}$=CH_2), 7.06 ppm (t, H-1). J (1/2) = 6.4, (CH_2-CH) = 7.4 Hz. Hydroquinone component: δ = 4.80 (s, broad, 2H), 6.70 (s, 4H). ^{13}C-NMR: δ = 27.9 (q, t-Bu), 50.3 (t, C-2), 60.2 (t, allyl), 71.3 (s, t-Bu), 121.5 (d, J = 188 Hz, C-1), 124.0 (d, allyl), 125.0 ppm (t, allyl). Hydroquinone component: 116.5 (d), 151.0 ppm (s).

2-tert-Butyl-3-oxa-7-thia-2-azabicyclo[3.3.0]octane-7,7-dioxide (**15e**): Nitrone **2e** was completely converted to **15e** after standing for four days at room temperature in chloroform. Colourless solid, m.p. 109°C from ethanol. $C_9H_{17}NO_3S$ Calcd 219.0924 Found 219.0923. High resolution MS (FD): m/e = 219 (M^+, 100%). ^{1}H-NMR: 1.13 (s, t-Bu), 3.00 (dd, H-6'), 3.15 (dd, H-8'), 3.25-3.34 (m, 3H, H-5, H-6 and H-8), 3.59 (dd, H-4'), 3.79 (ddd, H-1), 4.27 ppm (dd, H-4). J (1/5) (1/8) (1/8') = 8.7, 7.8 and 7.7; (4/4') = 8.7, (4/5) = 7.0, (4'/5) = 6.9, (5/6') = 12.6, (6/6') = 15.8, (8/8') = 14.2 Hz. ^{13}C-NMR: δ = 25.6 (q, t-Bu), 43.2 (d, C-5), 52.3 (t, C-6), 56.0 (t, C-8), 57.0 (d, C-1), 58.2 (s, t-Bu), 71.2 ppm (t, C-4).

1-(Allylsulfonyl)-2-[N-(4-tert-butylphenyl)hydroxyamino]ethane (**13g**) was prepared as described for the corresponding compounds **1**[1] in 84% yield. Colourless crystals, m.p. 99°C from diethyl ether. - $C_{15}H_{23}NO_3S$ (297.3) Calcd. C 60.59 H 7.80 N 4.71 Found C 60.67 H 7.81 N 4.75. MS (EI): m/e = 297 (M^+, 29%). ^{1}H-NMR: δ = 1.30 (s, t-Bu), 3.35 (t, 2H, H-1), 3.74 (t, 2H, H-2), 3.79 (d, 2H, C$\underline{H}_2$-CH=), 5.45 (m, 3H, -CH=C$\underline{H}_2$ and OH), 5.95 (m, 1H, -$\underline{C}$H=CH_2), 7.09-7.35 ppm (m, 4H, phenyl). J (1/2) = 6.6, (CH_2-CH=) = 7.1 Hz. ^{13}C-NMR: δ = 31.3 (q, t-Bu), 34.1 (s, t-Bu), 48.2 (t, C-2), 52.8 (t, C-1), 58.6 (t, allyl), 116.5 (d, Ph), 124.5 (d, allyl), 124.8 (t, allyl), 125.6 (d, Ph), 145.9 (s, Ph), 148.9 ppm (s, Ph).

2-(4-tert-Butylphenyl)-3-oxa-7-thia-2-azabicyclo[3.3.0]octane-7,7-dioxide (**15g**) was isolated from oxidation of **13g** by lead dioxide or by p-benzoquinone after 5 h as described for the other oxidations in 73% yield. Colourless solid, m.p. 195-197°C from diethyl ether. $C_{15}H_{21}NO_3S$ (295.3) Calcd. C 60.99 H 7.17 N 4.74 Found C 60.10 H 7.21 N 4.70. MS (EI): m/e = 295 (M^+, 47%). ^{1}H-NMR: δ = 1.30 (s, t-Bu), 3.14 (dd, H-6'), 3.21 (dd, H-8'), 3.42 (ddd, H-6), 3.49-3.55 (m, 2H, H-5 and H-8), 3.88 (dd, H-4'), 4.14 (dd, H-4),

4.58 (q, H-1), 6.92-7.35 ppm (m, 4H, Ph). J (1/5) = 8.0, (1/8) = 8.0, (1/8') = 8.0, (4/4') = 9.1, (4/5) = 6.8, (4'/5) = 2.5, (5/6) = 8.5, (5/6') = 9.4, (6/6') = 13.5, (6/8) = 2.5 Hz), (8/8') = 13.7 Hz. ^{13}C-NMR: δ = 31.4 (q, t-Bu), 34.2 (s, t-Bu), 43.5 (d, C-5), 53.6 (t, C-6), 53.9 (t, C-8), 64.5 (d, C-1), 71.4 (t, C-4), 115.1 (d, Ph), 126.1 (d, Ph), 145.9 (s, Ph), 146.2 ppm (s, Ph).

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