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Sulfonic Peracids - III.[1]
Heteroatom Oxidation and Chemoselectivity

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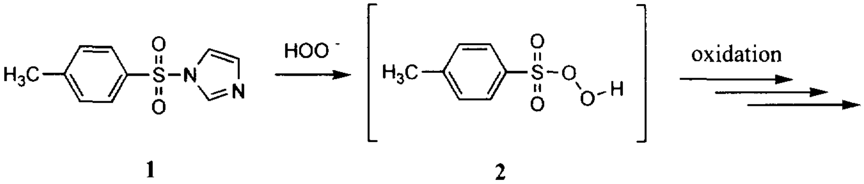
Abstract: We have investigated the *p*-toluenesulfonic peracid (**2**) generated *in situ* in the oxidation of different types of compounds containing nitrogen and/or sulfur. The sulfonic peracid **2** shows a remarkable chemoselectivity characterized by a preferred oxidation of sulfides to the sulfones in the presence of amines or olefins and a strong dependence on the nature of the amine in the competitive oxidation of olefins and amines.

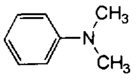
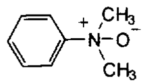
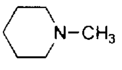
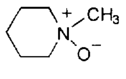
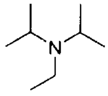
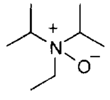
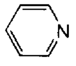
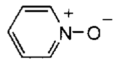
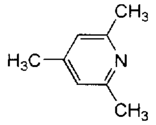
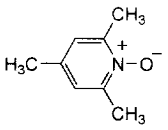
As described previously the sulfonic peracid **2** was generated *in situ* by the reaction of *p*-toluenesulfonylimidazole (**1**) with H_2O_2 in the presence of aqueous NaOH (scheme 1). It had been proven to be a powerful oxidant in the epoxidation of various olefins.[1,2] As a part of our ongoing investigation concerning the chemistry of sulfonic peracids generated *in situ* now we wish to report about the behaviour of this novel oxidant towards amines, azomethines and sulfides and its chemoselectivity.



Scheme 1

As expected the oxidation of tertiary amines **3a** - **e** with the oxidation system **1** / H_2O_2 / NaOH leads to the formation of the corresponding N-oxides **4a** - **e** in moderate to very good yields depending on the type of amine introduced (table 1). The N-oxides were transformed into the picrates[3] because of their easier isolation and greater stability and then characterized by standard methods. The yields of **4a** - **e** obtained with the oxidant **1** / H_2O_2 / NaOH are comparable to those reported previously for common oxidants like percarboxylic acids[3,4] or imidoperbenzoic acid.[5]

Table 1: Oxidation of Various Tertiary Amines with *p*-Toluenesulfonic Peracid (**2**)

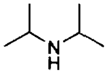
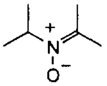
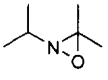
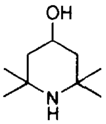
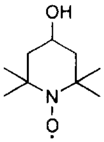
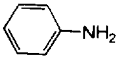
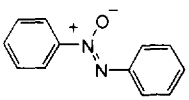
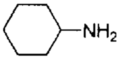
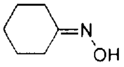
Entry	Amine	Product	Yield [%] [a]
1	 **3a**	 **4a**	95 [b]
2	 **3b**	 **4b**	70 [b]
3	 **3c**	 **4c**	40 [b, c]
4	 **3d**	 **4d**	60 [b]
5	 **3e**	 **4e**	55 [b]

a) Isolated yield of purified product with reference to starting material. b) Isolated in form of their picrates. c) see ref. 6.

The results obtained in the oxidation of secondary and primary amines selected with **2** were summarized in table 2. In detail, secondary amines like diisopropylamine (**5**) are oxidized mainly to the corresponding nitrone **6** *via* the diisopropylhydroxylamine which was detected by GLC/MS analysis (oxidation experiment with only one equivalent of **1**). ^{1}H NMR investigations of the crude product and of the purified product (Kugelrohr distillation) point to an equilibrium between the nitrone **6** and the isomeric oxaziridine **7** in a ratio of about **6** : **7** = 8 : 1.

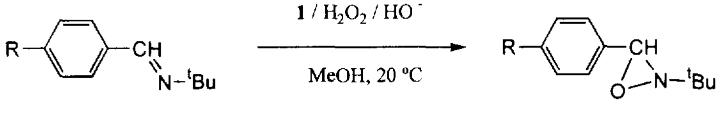
4-Hydroxy-2,2,6,6-tetramethylpiperidine (**8**) as an example for secondary amines having no α-hydrogens is oxidized to the nitroxyl radical **9** as described also for other peracid oxidations.[7] In contrast to this, recently it was reported that even with 4 equivalents caroate (Oxone®) almost no oxidation could be achieved with this type of amines.[8] Aniline (**10**) and cyclohexylamine (**12**) were investigated as representatives for primary amines yielding almost exclusively azoxybenzene (**11**) (yield 65%) and cyclohexanone oxime (**13**) (yield 60%) respectively, by applying 150 mol-% of the oxidant **1** / H_2O_2 / NaOH. The former oxidation leads to almost the same results (product and yield, table 2) as described for the system PhCN / H_2O_2 / base.[5] This result indicates the similar reactivity and oxidation power of both oxidants. In contrast to this the oxidation of primary aliphatic amines with dimethyldioxirane yields a multicomponent mixture of oxidation products.[9]

Table 2: Oxidation of Various Secondary and Primary Amines with **2**

Entry	Amine	Product	Yield [%] a)
1	 **5**	 +  (8 : 1) **6** **7**	55
2	 **8**	 **9**	70
3	 **10**	 **11**	65
4	 **12**	 **13**	66

a) Isolated yield of purified product with reference to starting material.

The oxidation of the azomethines **14 a-c** proceeds in a peracid-like manner yielding the oxaziridines **15 a-c** (scheme 2). Interestingly, in the case of the oxaziridine **15a** we could establish an *E/Z*-isomer ratio of about 15:1 determined by ^1H NMR spectroscopy at $\delta = 4.66$ ppm (*E*-isomer) and $\delta = 5.24$ ppm (*Z*-isomer) whilst the ^1H NMR spectra of the oxaziridines **15b** and **15c** showed only the C-H signals of the *E*-isomers which is in agreement with observations previously reported concerning the oxidation of **14b**.[10] The formation of the nitrone as byproduct only in the oxidation of **14c** was found as a result of the electron donating character of the CH_3O group.[11]



14 a - c **15 a - c**

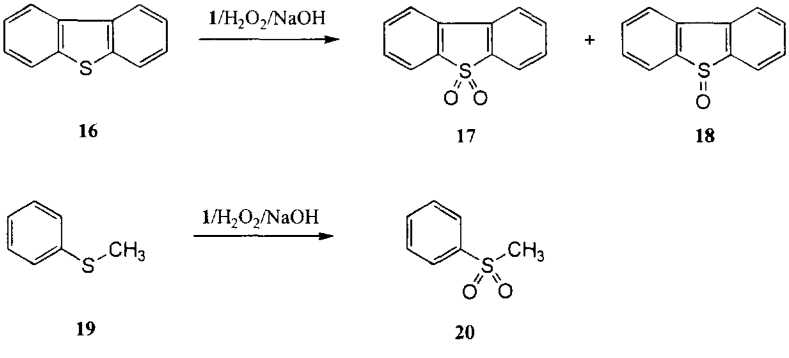
Scheme 2

Table 3: Oxidation of Substituted N-*tert.*-butyl-Benzaldimines **14 a - c** with **1** / H_2O_2 / HO^-

Entry	Azomethine	R	Oxaziridine	Yield [%] [a]
1	**14 a**	H	**15 a**	61 [b]
2	**14 b**	NO_2	**15 b**	75
3	**14 c**	CH_3O	**15 c**	38 [c]

a) Isolated yield of purified product with reference to starting material. b) *E/Z*-isomer ratio: 15 : 1. c) The isomeric nitrone is formed as byproduct (~ 5 %).

The reaction of sulfides with **1** / H_2O_2 / NaOH is illustrated in scheme 3 yielding mainly the corresponding sulfones. The sulfoxides as the intermediate products could be isolated only in very few cases. This shows the stronger oxidation power of **2** in comparison to common peroxy acids which rapidly oxidize sulfides to the corresponding sulfoxides at low temperatures but afford more drastic conditions for the conversion of sulfoxides to sulfones.[12]

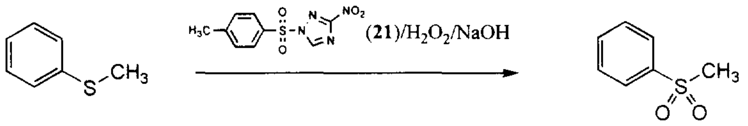


16 **17** **18**

19 **20**

Scheme 3

Because of the weakly alkaline medium (pH 8 ~ 9) during the reaction with the oxidation system **1** / H_2O_2 / HO^- we could not completely rule out the competitive oxidation of the intermediate sulfoxide to the corresponding sulfone by the HOO^- anion. For this reason the oxidation of **19** was carried out with the system *p*-toluenesulfonyl-3-nitro-1,2,4-triazole (**21**) / H_2O_2 / HO^- (known to proceed with a decreased pH ~ 5-6)[1] to exclude the possible side oxidation by the hydroperoxy anion HOO^- (scheme 4). As this oxidation led to nearly identical results we deduce that the only oxidizing agent is the *p*-toluenesulfonic peracid (**2**).

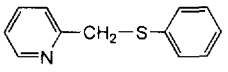
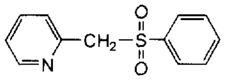
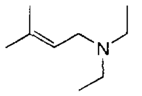
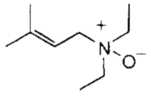
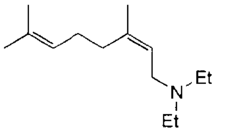
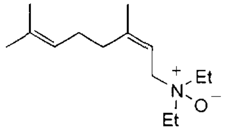
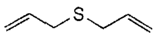
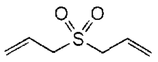
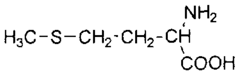
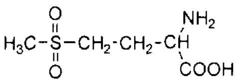


19 **20**

Scheme 4

For evaluating the chemoselectivity of the novel oxidant various compounds have been choosen with two different oxidizable moieties within the same molecule. The results of these experiments (table 4) show that, despite of its reactivity, the sulfonic peracid **2** generated *in situ* is a very chemoselective one. In the case of 2-[(phenylthio)methyl]pyridine[13] (**22**) the corresponding sulfone **23** was found as the sole product and no N-oxidation could be observed.[14] N,N-diethyl-N-(3-methylbut-2-en-1-yl)amine[15] (**24**) was not epoxidized at all and exclusively the N-oxide **25** was isolated as the MeOH adduct. Because the allylic double bond is deactivated due to the amino function we decided to investigate the N,N-diethyl nerylamine[15] (**26**) containing a second trisubstituted double bond isolated from the allyl amine part. However, there was no epoxidation and the N-oxide **27** was obtained in a similar yield to **25**. Concluding from these experiments the oxidation of diallyl sulfide (**28**) should result in a sulfur oxidation and, indeed, only the diallyl sulfone (**29**) was obtained in good yields. Contrary, the mCPBA oxidation of similar olefinic sulfides led not only to sulfones but also to products resulting from an oxidation of the double bond.[12] The advantage of **2** in comparison to the caroate as oxidizing agent is shown in the oxidation of L-methionine (**30**). While the oxidation of **30** with 3 equivalents $n\text{-}Bu_4N^+HSO_5^-$ could only be achieved after esterification of the carboxylic acid function in 33% yield (see ref. 13) the use of 1.5 equivalents of the oxidant **1** / H_2O_2 / NaOH renders the oxidation of **30** to **31** in 45% yield because of the weakly alkaline conditions.

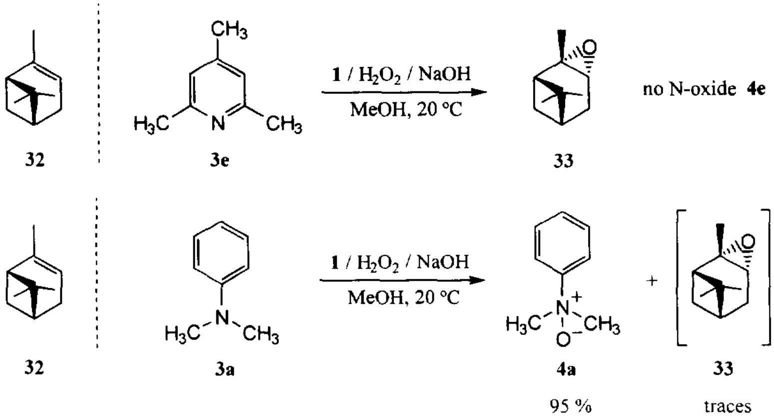
Table 4: Chemoselective Oxidation by the *p*-Toluenesulfonic Peracid (**2**)

Entry	Starting Material	Product	Yield [%] [a]
1	 **22**	 **23**	64
2	 **24**	 **25**	60
3	 **26**	 **27**	57
4	 **28**	 **29**	83
5	 $H_3C-S-CH_2-CH_2-CH(NH_2)COOH$ **30**	 $H_3C-\overset{O}{\underset{O}{S}}-CH_2-CH_2-CH(NH_2)COOH$ **31**	45

a) Isolated yield of purified product with reference to starting material.

Besides this the chemoselectivity of **2** was tested in competitive runs of different types of tertiary amines with the same olefin α-pinene (**32**, scheme 5) showing a remarkable differentiation between the different applied substrates. Obviously, from the results presented there is further evidence for the electrophilic character of the sulfonic peracid **2** demonstrated by the preferred oxidation of the more electron-rich amine **3a** in comparison to the electron-poor pyridine derivate **3e**.

Summarizing, the oxidation system **1** / H_2O_2 / NaOH has been proven to be a strong but very chemoselective oxidant in the oxidation of various compounds containing heteroatom functionalities. The chemoselectivity of *p*-toluenesulfonic peracid (**2**) is expressed by the order sulfur > *tert.* amines > olefins > pyridine N-atoms, thus allowing the selective conversion of sulfides into sulfones in the presence of other oxidizable functions within the same molecule. Additionally, the oxidant **2** provides access to oxidations that are not possible with caroate.



Scheme 5

EXPERIMENTAL PART

^1H NMR investigations were carried out on a Varian Gemini 300 (300 MHz) with hexamethyldisiloxane (HMDSO) as internal reference. GLC-MS analyses were performed on a Varian Saturn II spectrometer. Melting points were recorded on a Boetius Hotstage apparatus and are uncorrected. The purity of the compounds introduced was verified prior use by GLC or TLC. H_2O_2 was a commercial product and used as 33% (Merck) or 70% aqueous solution (Peroxid-Chemie GmbH). The content of peroxide was determined by iodometric titration before use. Solvents for column chromatography were purified and distilled prior use. 1-(4-Methylphenyl)sulfonylimidazole (**1**) was prepared according to Staab.[16] Compounds **3a-e,5,8,10,12,16,19,21,28,30** and **32** were commercially available products (Aldrich, Fluka). Compounds **14a-c**,[17] **22**,[13] **24**,[15] **26**[15] were prepared according to the literature.

General procedure for the oxidation of tertiary amines: 4 mmol of the tertiary amine, 6 mmol (0.667 g) *p*-toluenesulfonylimidazole (**1**) and 8 mmol H_2O_2 (33 %) were dissolved in 15 ml MeOH and 6 ml of 1N NaOH were added to the reaction mixture within 1 h with stirring. After stirring for further 30 min the reaction mixture was concentrated in vacuo, water was added and the unchanged amine extracted with ether. The aqueous phase was put into a boiling aqueous solution of 4.5 mmol (1.03 g) picric acid. The N-oxide picrate precipitated or crystallized on cooling and was recrystallized from EtOH to give the pure N-oxide picrate. N,N-dimethylaniline N-oxide (**4a**), picrate: 1.393 g (95 %), mp. 137 - 138 °C, lit.mp.[5] 138 - 139 °C. N-methylpiperidine N-oxide (**4b**), picrate: 0.964 g (70 %), mp. 180 - 183 °C, lit.mp.[18] 176 - 188 °C. Diisopropylethylamine N-oxide (**4c**), picrate: 0.599 g (40 %), mp. 198 - 202 °C (decomp.), ^1H NMR (acetone-d_6) δ [ppm]: 1.46 (t, 3H, J = 7.3 Hz), 1.54 (d, 12H, J = 6.6 Hz), 3.89 (quart, 2H, J = 7.3 Hz), 4.37 (sept, 2H, J = 6.6 Hz), 8.69 (s, 2H); elemental analysis: $C_{14}H_{22}N_4O_8$ (374.35) calc.: C, 44.92; H, 5.92; N, 14.97; found: C,45.22; H, 6.21; N,15.07 %. Pyridine N-oxide (**4d**), picrate: 0.778 g (60 %), mp. 167 - 168 °C, mixed mp. 167-168 °C (with an authentic sample prepared from commercial pyridine N-oxide (Aldrich) and picric acid). 2,4,6-Trimethylpyridine N-oxide (**4e**), picrate: 0.806 g (55 %), mp. 169 - 171 °C, elemental analysis:$C_{14}H_{14}N_4O_8$ (366.28) calc.: C, 45.91; H, 3.85; N, 15.30; found: C, 46.09; H, 4.28; N, 15.34 %.

Oxidation of diisopropylamine (5): To a stirred solution of 5 mmol (0.506 g) freshly distilled diisopropylamine (**5**), 10 mmol (2.222 g) **1** and 20 mmol H_2O_2 (33 %) 5 ml 2N NaOH were added within 1 hour. When **1** was completely consumed the reaction mixture was concentrated in vacuo, water was added and the mixture extracted with CH_2Cl_2. The organic phase was washed with saturated aq. $NaHCO_3$, water and brine and finally dried with $MgSO_4$. After evaporation of the solvent the crude product was chromatographed on alkaline alumina ($CHCl_3$/MeOH = 9 : 1) yielding 306 mg (55 %) of a mixture of the nitrone **6** and oxaziridine **7** (**6** : **7** = 8 : 1). After Kugelrohr distillation of the chromatographed product the colourless oil distilled showed the same ratio of **6** and **7** determined by measuring the integrals of the signals at δ = 2.12 ppm and δ = 1.85 ppm in the ^1H NMR spectrum. **6**: ^1H NMR ($CDCl_3$) δ [ppm]: 1.35 (d, 6H, J = 6.5 Hz), 2.12 (s, 3H), 2.14 (s, 3H), 4.45 (sept, 1H, J = 6.4 Hz). **7**: ^1H NMR ($CDCl_3$) δ [ppm]: 1.05 (d, 6H, J = 6.3 Hz), 1.85 (s, 3 H), 1.86 (s. 3H), 3.12 (sept, 1H, J = 6 Hz).

*Oxidation of 4-hydroxy-2,2,6,6-tetramethylpiperidine (**8**):* 5 mmol (0.786 g) **8**, 8 mmol (1.778 g) **1** and 10 mmol H_2O_2 (33 %) were dissolved in 15 ml MeOH and 4 ml 2N NaOH were added dropwise under stirring. After 2 h the reaction mixture was concentrated in vacuo, water was added and the mixture extracted several times with Et_2O. The organic phase was treated as described above to yield after evaporation of the solvent and recrystallization from n-hexane 600 mg (70 %) 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (**9**) as orange needles, mp. 69 °C (lit.mp.[7] 69 - 71 °C).

*Oxidation of aniline (**10**):* 2 mmol (186 mg) freshly distilled aniline (**10**), 4 mmol (0.888 g) **1** and 8 mmol H_2O_2 (33 %) were dissolved in 10 ml MeOH and 2 ml 2N NaOH were added to the reaction mixture within 1 h. After further 2 h stirring the mixture was extracted with toluene and the organic phase was dried with $MgSO_4$. After evaporation of the solvent the remaining dark-red oil was chromatographed on silica gel (EtOAc/n-hexane 1:1) yielding 128 mg (65 %) of azoxybenzene (**11**) as brownish crystals after crystallization from acetone/n-hexane, mp. 33 ° C, lit.mp.[5] 35.5 °C, mixed mp. 33 °C. GLC-MS (EI): 198 [M+].

*Oxidation of cyclohexylamine (**12**):* 2 mmol (198 mg) of **12**, 4 mmol (0.888 g) **1** and 8 mmol H_2O_2 (33 %) were dissolved in 10 ml MeOH. 2 ml 2N NaOH were added within 1 h with stirring. After complete consumption of **1** (TLC) the mixture was worked up in the usual way yielding pure cyclohexanone oxime (**13**) (152 mg, 66 %), mp. 89 °C, lit.mp. 90 °C.

*General procedure for the oxidation of azomethines **14 a-c**:* 1.5 ml 2N NaOH were added slowly to a methanolic solution containing 2 mmol of the azomethine, 4 mmol (0.888 g) **1** and 8 mmol H_2O_2 (33 %) at room temperature. After complete consumption of **1** the mixture was extracted with ether, the collected organic phases were washed with saturated aq. $NaHCO_3$, water and brine and dried over $MgSO_4$. After evaporation of the solvent the crude product was purified by column chromatography (silica gel, EtOAc/n-hexane 1:5) yielding the pure oxaziridines **15 a-c**. **15a**: 218 mg (61 %), colourless oil (mixture of *E/Z*-isomers: *E*:*Z* = 15:1). ^1H NMR ($CDCl_3$) δ [ppm]: 1.15 (s, 9H), 4.66 (s, 1H, *E*-isomer), 5.24 (s, 1H, *Z*-isomer), 7.32 - 7.44 (m, 5H). **15b**: 332 mg (75 %), yellowish needles, mp. 64.5 - 65 °C, lit.mp.[19] 65 °C.^1H NMR ($CDCl_3$) δ [ppm]: 1.17 (s, 9H), 4.74 (s, 1H), 7.59 (d, 2H, J = 8.4 Hz), 8.21 (d, 2H, J = 8.4 Hz). **15c**: 159 mg (38 %), colourless oil. ^1H NMR ($CDCl_3$) δ [ppm]: 1.14 (s, 9H), 3.78 (s, 3H), 4.61 (s, 1H), 6.87 (d, 2H, J = 7.6 Hz), 7.35 (d, 2H, J = 7.6 Hz). All data are in good agreement with those reported.[11]

*Oxidation of dibenzothiophene (**16**):* 1 mmol (184 mg) **16**, 2 mmol (0.444 g) **1** and 4 mmol H_2O_2 (70 %) were dissolved in 10 ml ^{t}BuOH at room temperature. 1 ml of 2N NaOH was added dropwise to this mixture and the proceeding of the reaction was controlled by TLC until **1** was completely consumed. The mixture was extracted with ether and worked up in the way described above. After evaporation of the solvent the crude product was chromatographed on silica gel (EtOAc/n-hexane 1:1) to yield 77 mg (42 %) unchanged **16** followed by 108 mg (50 %) dibenzothiophene sulfone (**17**) and 16 mg (8 %) dibenzothiophene sulfoxide (**18**). The identity of the oxidation products was confirmed by the determination of their melting points as well as the mixed melting points with authentic samples (**17**: Aldrich, **18**: prepared by oxidation of **16** with acetic acid/H_2O_2). **17**: mp. 231 - 233 °C, mixed mp. 231 - 233 °C. **18**: mp. 189 - 191 °C, mixed mp. 189 - 190 °C.

*Oxidation of phenylmethyl sulfide (**19**):* 2 mmol (248 mg) phenylmethyl sulfide (**19**) were oxidized with 4 mmol (0.888 g) **1**, 8 mmol H_2O_2 (70 %) and 2 ml 2N NaOH in the same way as described for for the oxidation of **16**. After usual work up (CH_2Cl_2 was used in the extraction step instead of ether) the phenylmethyl sulfone (**20**) was obtained as the sole product in 68 % yield (212 mg). The product was identified by its melting point (85-87 °C) and mixed mp. (86-87 °C) with an authentic sample (Fluka).

Oxidation of phenylmethyl sulfide (19) with p-toluenesulfonyl-3-nitro-1,2,4-triazole (21)/H_2O_2/NaOH: 1 mmol (124 mg) **19**, 2 mmol (0.536 g) **21** and 4 mmol H_2O_2 (70 %) were dissolved in 5 ml THF and cooled down to -5 °C. Then 0.5 ml 2N NaOH were added dropwise with stirring until **21** was completely consumed (TLC). After evaporation of the THF brine and CH_2Cl_2 were added and the mixture extracted several times. After drying with $MgSO_4$ and evaporation of the solvent **20** was obtained as white crystals (114 mg, 73 %), mp. 85-87 °C.

Oxidation of 2-[(phenylthio)methyl]pyridine (22): As described above 4 mmol (0.888 g) **1**, 8 mmol H_2O_2 (33 %) and 2 ml 2N NaOH were used for the oxidation of 2.5 mmol (0.503 g) 2-[(phenylthio)methyl]pyridine (**22**)[13] in MeOH. After the usual work up 373 mg (64 %) of the 2-[(phenylsulfonyl)methyl]pyridine (**23**) were obtained as the sole product; white crystals, mp. 111 - 112 °C, lit.mp.[13] 111 - 112 °C.

Oxidation of N,N-diethyl(2-methylbut-2-enyl)amine (24): 2 mmol (0.282 g) **24**, 3 mmol (0.667 g) **1** and 4 mmol H_2O_2 (33 %) were dissolved in 10 ml MeOH at room temperature and 1.5 ml 2N NaOH were added slowly with stirring. After consumption of **1** (TLC) the reaction mixture was concentrated in vacuo and extracted several times with ether. GLC analysis of the ether extract showed only few unchanged material. The aqueous phase was concentrated to dryness and the resulting solid was dissolved/suspended in $CHCl_3$, filtered and the $CHCl_3$ evaporated to yield 270 mg oily crude product. After column chromatography on neutral alumina ($MeOH/CHCl_3$ 1:7) 178 mg (55 %) N,N-diethyl-N-(3-methylbut-2-en-1-yl)amine N-oxide (**25**) were isolated as MeOH adduct. ^1H NMR ($CDCl_3$) δ [ppm]: 1.31 (t, 6H, J = 7.1 Hz), 1.71 (s,3H), 1.80 (s, 3H), 3.14 (quart, 4H, J = 7.1 Hz), 3.41 (s, 3H, CH_3OH), 3.73 (d, 2H, J = 7.4 Hz), 5.35 (t (br), 1 H, J = 7.4 Hz).

Oxidation of N,N-diethyl(3,7-dimethylocta-cis-2,6-dien-1-yl)amine (26): The oxidation of 2 mmol (0.429 g) **26** was carried out with 3 mmol (0.667 g) **1** and 4 mmol H_2O_2 (33 %) and worked up analogous as described for the oxidation of **24**. GLC-MS analysis of the ether extract showed only some unchanged material and no oxidation products. The evaporation of the organic phase gave 50 mg of **26** recovered. The aqueous phase was concentrated to dryness, dissolved/suspended in 10 ml $CHCl_3$ and filtered. The clear solution was evaporated to yield 420 mg of crude product which gave 259 mg (57 %) N,N-diethyl-N-(3,7-dimethylocta-*cis*-2,6-dien-1-yl)amine N-oxide (**27**) as MeOH adduct (colourless oil) after column chromatography on silica gel ($MeOH/CHCl_3$ 1:5). ^1H NMR ($CDCl_3$) δ [ppm]: 1.31 (t, 6H, J = 7.1 Hz), 1.57 (s, 3H), 1.65 (s, 3H). 1.80 (s, 3H), 2.09 (s (br), 4H), 3.17 (quart, 4H, J = 7.1 Hz), 3.42 (s, 3H, CH_3OH), 3.75 (d, 2H, J = 7.2 Hz), 5.02 (s (br), 1H), 5.41 (t, 1H, J = 7.1 Hz).

Oxidation of diallyl sulfide (28): 1 mmol (114 mg) diallyl sulfide (**28**), 2 mmol (0.444 g) **1** and 4 mmol H_2O_2 (70 %) were dissolved in 10 ml ^{t}BuOH. Then 1 ml of 2N NaOH was added dropwise to the mixture with stirring. After consumption of **1** the mixture was worked up in the usual way. Evaporation of the solvent (Et_2O) gave 120 mg (82 %) of the diallylsulfone (**29**) as colourless oil (garlic-like smell). ^1H NMR ($CDCl_3$) δ [ppm]: 3.69 (d, 4H, J = 7.3 Hz), 5.44 (m, 4H), 5.90 (m, 2H). GLC-MS (EI): 146 [M+].

Oxidation of L-methionine (30): 2 mmol (298 mg) **30**, 3 mmol (0.667 g) **1** and 4 mmol H_2O_2 (33 %) were dissolved in 15 ml $MeOH/H_2O$ (1:1) until a clear solution was obtained. Then 1.5 ml 2N NaOH were added dropwise to the reaction mixture over a period of 2 h. After stirring overnight a white solid had preticipated from the solution which was isolated and dried yielding 164 mg (45 %) of a silky white solid identified as L-methionine sulfone (**31**) compared with an authentic sample (Fluka) by its melting point and by qualitative paper chromatography (partial acetylated cellulose; n-butanol/glacial acetic acid/H_2O 4:1:1; N-CN indicator[20]), mp. 255 - 260 °C (decomp.). ^1H NMR (D_2O) δ [ppm]: 2.06 (m, 2H), 2.84 (s, 3H), 3.12 (m, 2H), 3.59 (t, 1H, J = 6.3 Hz).

Competitive oxidation experiments:

2 mmol (273 mg) α-pinene (**32**), 2 mmol (0.242 g) freshly destilled N,N-dimethylaniline (**3a**), 3 mmol (0.667 g) **1** and 4 mmol H_2O_2 (33 %) were dissolved in 10 ml MeOH. 1.5 ml 2N NaOH were added slowly to the reaction mixture so that the pH did not exceed a value of 8 - 9. When the addition of base was completed the reaction was terminated and the mixture extracted with ether. The organic phase was dried with $MgSO_4$ and analyzed by GLC-MS showing mainly **32** and only traces of α-pinene oxide (**33**) among with few unchanged **1**. Transferring

the aqueous phase into a boiling solution of 2.5 mmol (0.572 g) picric acid yielded 696 mg (95 %) of N,N-dimethylaniline N-oxide (**4a**) as picrate.

2 mmol (273 mg) α-pinene (**32**) and 2 mmol (0.242 g) 2,4,6-trimethylpyridine (**3e**) were oxidized with 3 mmol (0.667 g) **1** and 4 mmol H_2O_2 (33 %) in 10 ml MeOH. After the addition of 1.5 ml 2N NaOH the mixture was worked up as described above. GLC-MS analysis revealed the presence of **3e** and α-pinene oxide (**33**) in the organic phase among with some unchanged **1**. After evaporation of the solvent the crude reaction product (0.464 g) was analyzed by ^{1}H NMR spectroscopy indicating a ratio of **3e** : **33** ≈ 3 : 2 by measuring the integrals at δ = 0.91 ppm (CH_3 group of **33**) and δ = 2.23 ppm (4-CH_3 group of **3e**) and δ = 3.05 ppm (epoxy-H of **33**) and δ = 6.76 ppm (aromatic H of **3e**), respectively. The N-oxide **4e** could not be detected in the organic or aqueous phase.

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