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Unexpected Deoxygenation of 2,2,6,6-Tetramethylpiperidine-1-Oxyl (TEMPO) by Thiyl Radicals through the Formation of Arylsulphinyl Radicals

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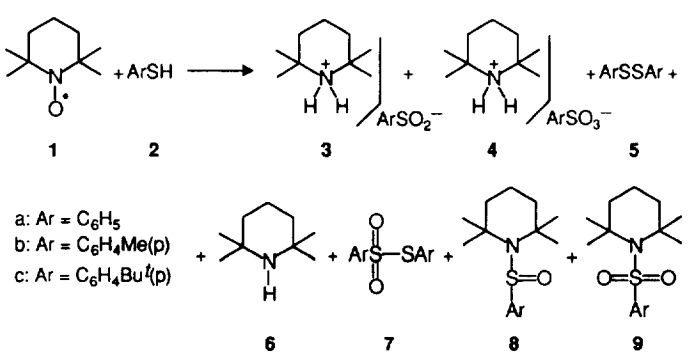
Abstract: 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO), upon reaction with thiophenols, undergoes deoxygenation leading mainly to the formation of tetramethylpiperidinium arylsulphinates and arylsulphonates. Other identified products of the reaction are aryldisulphides, 2,2,6,6-tetramethylpiperidine, S-aryl-arylthiosulphonates, N-arylsulphinyl- and N-arylsulphonyl-2,2,6,6-tetramethylpiperidine. The formation of the reaction products is discussed on the basis of the interaction of arylsulphinyl and arylsulphonyl radicals with TEMPO as well as on the basis of the evolution of the arylsulphinyl radical itself.

It is well known that aminoxyls can be reduced to the corresponding hydroxylamines by various reducing agents such as hydrazines, alkyl-, aryl-hydrazines and dihydropyridines, and that they can also remove hydrogen atoms from activated alkyl groups, for example, from alkylbenzenes.[1] Aminoxyls also undergo reduction to hydroxylamines by $NaBH_4$[2] whereas with $LiAlH_4$ they may be reduced to the corresponding amines,[3] as in their treatment with iron powder in boiling acetic acid.[4] Aminoxyls also undergo reduction[5] or deoxygenation reduction with hydrogen chloride.[6]

On the basis of the reactivity of aminoxyls towards good hydrogen donors, we studied the reaction of TEMPO (**1**) with thiophenols expecting to obtain the hydroxylamine corresponding to TEMPO and arylthiyl radicals, which could dimerize to aryldisulphides or couple with TEMPO to afford a TEMPO-arylthiyl adduct, but this adduct was never isolated. Even if the reaction of 3-aminocarbonyl-2,2,5,5-tetramethyl-pyrrolinyl-1-oxide with compounds bearing a sulfhydryl group has been reported to form sulphonic acids, no clear data were described for such a reaction.[7] The results described here give a complete picture of the reactivity of arylthio radicals with aminoxyls and new insights on the synergism of disulphides and secondary amines in polymer stabilization. In fact it is



Scheme 1

well known that these amines exert their stabilizing properties through the intermediate formation of the corresponding aminoxyls and sulphides like dilaurylthiodipropionate through sulphinyl radical.[8]

RESULTS

The reactions of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (**1**) with thiophenols (**2a-c**) were performed in benzene at room temperature under nitrogen in 2:1 ratio, respectively. The 2,2,6,6-tetramethylpiperidinium arylsulphinates (**3**) and arylsulphonates (**4**) precipitated in the reaction medium after concentration under reduced pressure and were separated by filtration, whereas compounds **5-9** were separated by chromatography from the filtrate. All the isolated products are shown in Scheme 1 and their yields are reported in Table 1.

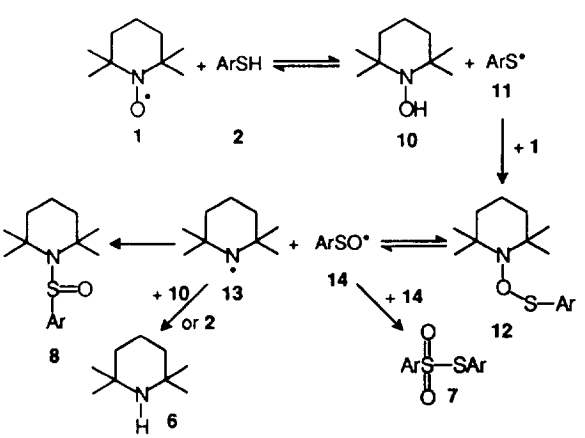
Table 1. Percentages Yields of Products of the Reaction Between **1** and **2**.[a]

Reagents	Products (%)						
	3	**4**	**5**	**6**	**7**[b]	**8**	**9**
1 + **2a**	14	49	8	9	traces	5	7
1 + **2b**	21	47	12	7	traces	4	6
1 + **2c**	9	56	10	10	traces	5	6

[a], The yields are referred to thiophenol (**2**) except for compound **6** (referred to TEMPO); [b], detected by GC-MS.

Compounds **3a-4a**, **3b-4b** (which precipitated as a mixture of the two salts) were identified by comparison with authentic samples prepared starting from the appropriate sulphinic and sulphonic acids with tetramethylpiperidine. On the other hand, compounds **3c** and **4c** were identified by comparing the ^{1}H NMR spectrum of their mixture with the spectra of compounds **3b** and **4b** (in fact, the aromatic region of **3b** is characterized by two doublets at $\delta = 7.2$ and $\delta = 7.6$), since their corresponding sulphinic and sulphonic acids were unavailable. The sulphonate **4c** was the only product isolated from the salts mixture by crystallization from CH_3CN while the sulphinate **3c**, owing to its small amount, was never isolated in a pure state. The ratios of salts **3** and **4** were measured by ^{1}H NMR and are shown in Table 1.

Compounds **5a** and **5b** were identified by comparison of their spectroscopic data with authentic commercial samples while compound **5c** was characterized through its ^{1}H NMR and mass spectra and elemental analyses. Compounds **6** and **7a** were also identified by comparison with authentic commercial samples. Compound **7b** was identified by comparing its spectroscopic data with an authentic sample prepared according to the literature.[9] Compound **7c** was identified by comparing its spectroscopic data with a sample prepared according to the same literature method and was characterized by ^{1}H NMR, IR, mass spectra and elemental analyses. Compounds **8** and **9** gave misleading spectroscopic data. In particular, compounds **8a-c** gave very clear mass spectra with a fragmentation in agreement with the reported structure: in all cases the main ion peak was that corresponding to the ArSO group, which was also present in the IR spectra at *ca.* 1050 cm^{-1}.[10,11] However their ^{1}H and ^{13}C NMR spectra showed very broad signals for piperidine protons and carbons respectively, with a different pattern compared to compounds **3**, **4** and **9**. These unusual NMR spectra were due to the partial N-S double bond character which gives rise to restricted rotation rendering each methyl non equivalent. In fact, upon heating a solution of compound **8c** in DMSO-d_6, the signals became sharper and similar to those observed for compounds



Scheme 2

Table 2. Selected Bond Distances (Å), Angles (°) and Torsion Angles (°) with e.s.d.'s in Parentheses.

Compound	8b	9c	
		Mol. 1	Mol. 2
S(1)-O(1)	1.485(2)	1.468(9)	1.452(10)
S(1)-O(2)		1.413(9)	1.421(10)
S(1)-N(1)	1.675(2)	1.616(8)	1.655(8)
S(1)-C(10)	1.801(3)	1.795(11)	1.758(10)
N(1)-C(1)	1.518(4)	1.558(13)	1.538(12)
N(1)-C(5)	1.513(3)	1.534(14)	1.525(12)
C(1)-C(2)	1.537(5)	1.516(19)	1.530(18)
C(2)-C(3)	1.513(5)	1.521(22)	1.514(18)
C(3)-C(4)	1.501(6)	1.508(21)	1.532(18)
C(4)-C(5)	1.536(5)	1.474(17)	1.520(17)
C(13)-C(16)	1.503(6)	1.588(15)	1.532(12)
C(16)-C(17)		1.541(17)	1.552(19)
C(16)-C(18)		1.573(18)	1.500(16)
C(16)-C(19)		1.484(19)	1.562(32)
O(1)-S(1)-O(2)		117.4(5)	115.3(6)
O(1)-S(1)-N(1)	113.5(1)	109.2(4)	109.7(4)
O(1)-S(1)-C(10)	105.1(1)	106.6(4)	107.1(5)
O(2)-S(1)-N(1)		109.7(5)	112.5(5)
O(2)-S(1)-C(10)		106.1(5)	106.7(5)
N(1)-S(1)-C(10)	101.4(1)	107.3(4)	104.9(4)
S(1)-N(1)-C(1)	119.4(2)	116.4(6)	118.6(6)
S(1)-N(1)-C(5)	111.1(2)	120.3(6)	117.0(6)
C(1)-N(1)-C(5)	119.9(2)	120.5(8)	120.9(7)
N(1)-C(1)-C(2)	107.7(2)	107.5(9)	109.6(8)
C(1)-C(2)-C(3)	113.2(3)	112.7(12)	114.4(11)
C(2)-C(3)-C(4)	108.7(3)	106.1(12)	107.8(10)
C(3)-C(4)-C(5)	114.8(3)	113.2(11)	114.7(10)
N(1)-C(5)-C(4)	108.0(2)	110.9(9)	111.4(9)
S(1)-C(10)-C(11)	119.1(2)	116.4(7)	115.7(8)
S(1)-C(10)-C(15)	121.4(2)	124.4(8)	125.8(8)
C(12)-C(13)-C(16)-C(17)		-82.0(13)	86.1(12)
C(12)-C(13)-C(16)-C(18)		35.0(14)	-33.5(12)
C(12)-C(13)-C(16)-C(19)		151.9(12)	-160.4(14)

3, **4** and **9**. This behaviour is also known for N-nitrosoamines.[12] Compounds **9a-c** gave very clear ^1H and ^{13}C NMR spectra, which were consistent with the assigned structure, but their mass spectra did not show the molecular ion peak, being that observed 15 mass units lower; the appropriate molecular ion peak was only observed using a low electron energy (30 eV). The discrepancies observed in the spectroscopic data of compounds **8** and **9**, which all gave a very similar behaviour, were overcome by the X-ray analyses of compounds **8b** and **9c** (Figure 1 and 2). Selected bond distances, angles and torsion angles are reported in Table 2. The geometry of compound **8b** and **9c** is similar in the solid state: the benzene rings are planar within the experimental errors and the angles they form with the planar moiety C(1), C(2), C(4), C(5) of the piperidine ring is 104.2(1)° in **8b** and 92.1(4) and 91.2(4)° in molecule 1 and 2 of **9c**. The two symmetry-independent molecules in compound **9c** differ only in the conformation of the *tert*-butyl group with respect to the benzene ring, as can be seen from the torsion angles reported in Figure 2. Packing is consistent with van der Waals interactions.

DISCUSSION

As stated in the introduction, the purpose of this work was to study the interaction of TEMPO (**1**) with arylthiyl radicals (**11**). The molecular ratio 2:1 of TEMPO with thiophenols was chosen with the aim of generating a thiyl radical *via* hydrogen abstraction on thiophenols by one mole of TEMPO, and trapping the thiyl radical with a second mole of TEMPO. Even though adduct **12** (Scheme 2) was never isolated, it could readily form through the steps reported in Scheme 2, followed by decomposition to piperidinyl **13** and arylsulphinyl **14** radicals. The facile homolysis of the oxygen-nitrogen bond in adduct **12** may be supported by the fact that the same bond in arylsulphinyl nitrate[13] or in the pyridine N-oxide-arylsulphenyl chloride adduct[14] behaves in a similar way.

The first radicals formed (**11**) can dimerize to aryldisulphides **5**. Instead, arylsulphinyl radicals **14**, which are π-type radicals,[15] may couple with themselves to give S-aryl-arylthiosulphonates **7** or they can couple with the piperidinyl radical **13** to form compounds **8**. Piperidinyl radical **13** could also be reduced to **6** by thiophenol **2** or hydroxylamine **10**, formed in the first step of the reaction.

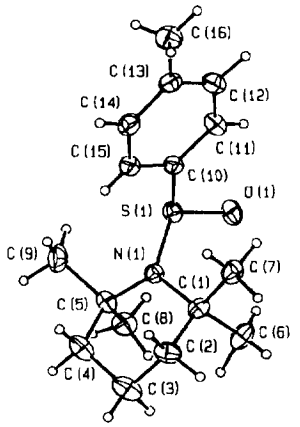


Figure 1
ORTEP drawing of the X-ray structure of **8b**.

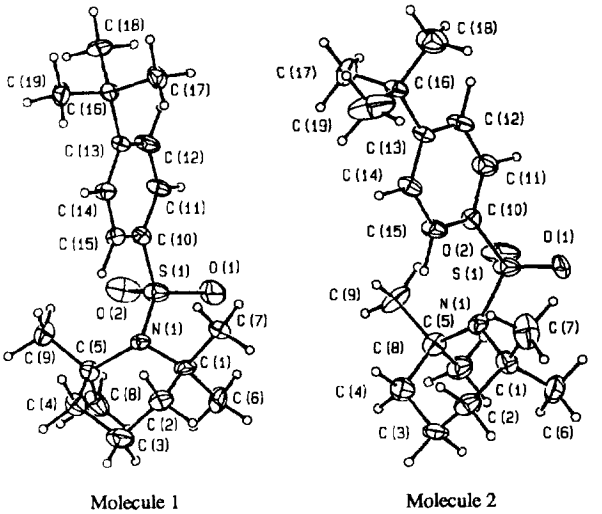


Figure 2
ORTEP drawing of the X-ray structure of **9c**.

Furthermore, arylsulphinyl radicals **14** may disproportionate to arylthiyl radicals **11** and arylsulphonyl radicals **15** as shown in Eq. (1).[16,17]

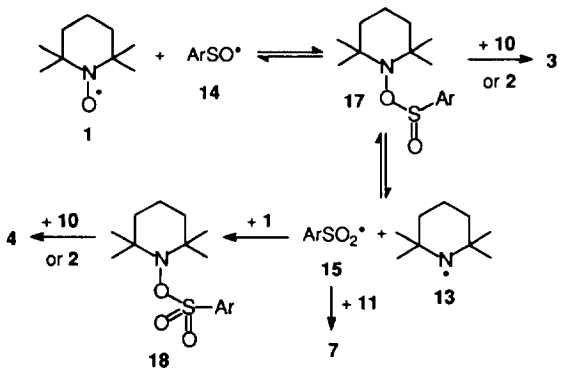
$$2\ ArSO^{\bullet}\ (\mathbf{14}) \longrightarrow ArS^{\bullet}\ (\mathbf{11}) + ArSO_2^{\bullet}\ (\mathbf{15}) \quad (1)$$

The formation of arylsulphonyl radicals **15** in the presence of reducing agents such as hydroxylamines **10** or thiophenols **2** may explain the formation of the arylsulphinic acids and thus the piperidinium sulphinates **3**, the yields of which are lower than those of sulphonates **4** as indicated in Table 1. The reason why sulphinates **3** form in lower yields than sulphonates **4** could be due to the fact that sulphonyl radicals **15**, which are σ-type radicals,[15] disproportionate faster than arylsulphinyl radicals **14** according to equation (2) proposed years ago by Waters et al.[18-20] and more recently by Gilbert[16] and others.[21]

$$2\ ArSO_2^{\bullet}(\mathbf{15}) \longrightarrow ArSO^{\bullet}\ (\mathbf{14}) + ArSO_2O^{\bullet}\ (\mathbf{16}) \quad (2)$$

The arylsulphonyloxy radicals **16** may justify the formation of piperidinium sulphonates **4**. Previously, it was proposed[18] that sulphonyl and sulphonyloxy radicals give rise to the formation of sulphonic acid anhydrides, which react with aniline to give anilinium sulphonates. For the reaction here described, we are not able to distinguish if the piperidinium sulphonate involves the sulphonic acid anhydride or the sulphonic acid itself. Even if the formation of sulphinates **3** and sulphonates **4** could be easily justified by the above mentioned literature reports, it is our opinion that the mechanisms shown in Scheme 3 could also be taking part in our reactions, above all for the sulphonates formation.

In fact the σ-type arylsulphonyl radicals **15** could form adducts **18** faster than the more stable π-type sulphinyl radicals **14** form adducts **17**. The mechanisms reported in Scheme 3, at least for the formation of adduct **18** could also be supported by the fact that arylsulphonyl radicals originated by photolysis of *p*-toluenesulphonyl chloride in methanol in the presence of TEMPO led to the formation of a mixture of sulphonate **4b** and of tetramethylpiperidinium chloride, which were identified by comparison with authentic samples (see experimental).



Scheme 3

EXPERIMENTAL

Melting points are uncorrected. IR were recorded on a Perkin-Elmer model 298 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ solution on a Varian Gemini 200 spectrometer (δ in ppm referred to Me_4Si). Mass spectra were recorded on a Carlo Erba QMD 1000 spectrometer. Elemental analyses of new crystalline compounds were performed with a Carlo Erba CHNSO E.A. 1108 elemental analyser. The light induced reaction was carried out using a 500 Watts mercury lamp. TEMPO (**1**), thiophenols (**2a-c**), aryldisulphides (**5a,b**), tetramethylpiperidine (**6**), S-phenyl-benzenethiosulphonate (**7a**), sodium benzenesulphinate and sodium *p*-toluenesulphinate, benzenesulphonic acid and *p*-toluenesulphonic acid, *p*-toluenesulphonyl chloride and solvents were all Aldrich commercial reagent grade products. S-(*p*-Tolyl)-*p*-toluenethiosulphonate (**7b**) was prepared according to the literature[9].

Reaction of TEMPO (1) with thiophenols (2a-c). General procedure

A solution of TEMPO (0.47 g, 3 mmol) in 6 ml of benzene and a solution of thiophenol (1.5 mmol) in 4 ml of benzene were separately placed into the two legs of an inverted Y flask, degassed with nitrogen for 15 mins and then mixed at room temperature. Upon mixing, the orange colour of TEMPO becomes immediately lighter. The mixture was left to react for 30 mins, evaporated under reduced pressure and taken up with benzene, from where the salts **3** and **4** were separated by filtration. The filtrate was then chromatographed on silica-gel column eluting with ethyl acetate/cyclohexane 1:9 and products were isolated in the following order: **5**, **9**, **8** and **6**. The isolated products were further purified on silica-gel preparative plates eluting with acetate/cyclohexane 1:9 or 2:8. Compounds **7** were detected only by GC-MS and identified by comparison with authentic sample.

2,2,6,6-Tetramethylpiperidinium p-tert-butylbenzenesulphinate (3c): ^1H NMR δ = 1.32 (9H, s), 1.44 (12H, s), 1.58 (6H, s) 7.41 (2H, d, *J* = 8.4 Hz), 7.64 (2H, d, *J* = 8.4 Hz).

2,2,6,6-Tetramethylpiperidinium p-tert-butylbenzenesulphonate (4c): mp 251-252 °C from CH_3CN; ^1H NMR δ = 1.32 (9H, s), 1.49 (12H, s), 1.63 (6H, s), 7.41 (2H, d, *J* = 8.8 Hz), 7.81 (2H, d, *J* = 8.8 Hz). Anal. Calcd. for $C_{19}H_{33}NO_3S$: C, 64.19; H, 9.36; N, 3.94; S, 9.00. Found: C, 64.22; H, 9.38; N, 3.97; S, 9.05.

p-tert-Butylphenyldisulphide (5c): mp 85-86 °C from ethyl acetate; ^1H NMR δ = 1.31 (18H, s), 7.33 (4H, d, *J* = 8.6 Hz), 7.45 (4H, d, *J* = 8.6 Hz); IR ν_{max} 1260, 1105, 1000 cm^{-1}; MS *m/z* (rel int) 330 (M^+, 73) 315 (100). Anal. Calcd. for $C_{20}H_{26}S_2$: C, 72.69; H, 7.94; S, 19.37. Found: C, 72.72; H, 7.96; S, 19.38.

N-Benzenesulphinyl-2,2,6,6-tetramethylpiperidine (8a): mp 74-75 °C from ethyl acetate; ^1H NMR δ = 0.92 (3H, br-s), 1.60 (15H, br-m), 7.42 (3H, m), 7.68 (2H, m); ^{13}C NMR δ = 17.7, 28.4, 29.2, 33.0, 35.8, 41.8, 43.9, 59.2, 61.8, 126.4, 129.0, 129.8, 150.7; IR ν_{max} 1240, 1125, 1075, 1050 cm^{-1}; MS *m/z* (rel int) 265 (M^+, 8) 250 (M^+ -15, 98), 125 (100). Anal. Calcd. for $C_{15}H_{23}NOS$: C, 67.89; H, 8.74; N, 5.28; S, 12.06. Found: C, 67.95; H, 8.76; N, 5.26; S, 12.09.

N-(p-Toluenesulphinyl)-2,2,6,6-tetramethylpiperidine (8b): mp 70-71 °C from ethyl acetate; ^1H NMR δ = 0.92 (3H, br-s), 1.60 (15H, br-m), 2.39 (3H, s), 7.24 (2H, d, *J* = 8.3 Hz), 7.54 (2H, d, *J* = 8.3 Hz); IR ν_{max} 1240, 1125, 1080, 1050 cm^{-1}; MS *m/z* (rel int) 279 (M^+, 2), 264 (M^+ -15, 20), 139 (100). Anal. Calcd. for $C_{16}H_{25}NOS$: C, 68.78; H,. 9.03; N, 5.02; S, 11.45. Found: C, 68.84; H, 9.05; N, 5.05; S, 11.49.

N-(p-tert-Butylbenzenesulphinyl)-2,2,6,6-tetramethylpiperidine (8c): mp 55-56 °C from ethyl acetate; ^1H NMR δ = 0.92 (3H, br-s), 1.34 (9H, s), 1.60 (15H, br-m), 7.46 (2H, d, *J* = 8.7 Hz), 7.59 (2H, d, *J* = 8.7 Hz);

IR ν_{max} 1240, 1125, 1080, 1060 cm^{-1}; MS *m/z* (rel int) 321 ($M^{+\cdot}$ 12), 306 (M^{+}-15, 93), 181 (100). Anal. Calcd. for $C_{19}H_{31}NOS$: C, 70.98; H, 9.73; N, 4.36; S, 9.95. Found: C, 70.88; H, 9.75; N, 4.38; S, 9.97.

*N-Benzenesulphonyl-2,2,6,6-tetramethylpiperidine (**9a**)*: mp 125-126°C from ethyl acetate; ^1H NMR δ = 1.58 (12H, s), 1.67 (6H, s), 7.47 (3H, m), 7.86 (2H, m); ^{13}C NMR δ = 17.2, 31.5, 44.3, 61.3, 126.5, 129.0, 131.7, 147.7; IR ν_{max} 1365, 1305, 1135 cm^{-1}; MS *m/z* (rel int) 266 (M^{+}-15, 45), 141 (M^{+}-140, 40), 109 (100). Anal. Calcd. for $C_{15}H_{23}NO_2S$: C, 64.02; H, 8.24; N, 4.98; S, 11.37. Found: C, 64.10; H, 8.26; N, 4.97; S, 11.40.

*N-(p-Toluenesulphonyl)-2,2,6,6-tetramethylpiperidine (**9b**)*: mp 118-119°C from ethyl acetate; ^1H NMR δ = 1.58 (12H, s), 1.66 (6H, s), 2.40 (3H, s), 7.24 (2H, d, J = 8.4 Hz), 7.73 (2H, d, J = 8.4 Hz); IR ν_{max} 1365, 1305, 1135 cm^{-1}; MS *m/z* (rel int) 280 (M^{+}-15, 49), 155 (M^{+}-140, 45), 109 (100). Anal. Calcd. for $C_{16}H_{25}NO_2S$: C, 65.05; H, 8.54; N, 4.74; S, 10.83. Found: C, 65.13; H, 8.52; N, 4.78; S, 10.85.

*N-(p-tert-Butylbenzenesulphonyl)-2,2,6,6-tetramethylpiperidine (**9c**)*: mp 115-116°C from ethyl acetate; ^1H NMR δ = 1.33 (9H, s), 1.58 (12H, s), 1.67 (6H, s), 7.45 (2H, d, J = 8.7 Hz), 7.78 (2H, d, J = 8.7 Hz); IR ν_{max} 1370, 1310, 1135 cm^{-1}; MS *m/z* (rel int) 322 (M^{+} -15, 98), 197 (M^{+} -140, 76), 109 (100). Anal. Calcd. for $C_{19}H_{31}NO_2S$: C, 67.61; H, 9.27; N, 4.15; S, 9.48. Found: C, 67.68; H, 9.30; N, 4.17; S, 9.50.

*Synthesis of tetramethylpiperidinium benzenesulphinates **3a** and **3b***

Benzenesulphinic and *p*-toluenesulphinic acids were prepared by adding 16% HCl (1 ml) to 3 mmoles of the corresponding sodium salts dissolved in 10 ml water under magnetic stirring. The solutions were then extracted with benzene, dried over Na_2SO_4 and concentrated under reduced pressure. The residue containing the appropriate acid was dissolved in 10 ml CH_3CN and then added to a solution of tetramethylpiperidine (0.42 g, 3 mmol) in 5 ml CH_3CN under magnetic stirring. The salts **3a** and **3b** precipitated immediately from the reaction mixture in quantitative yield. They were filtered and purified by crystallization from CH_3CN.

*2,2,6,6-Tetramethylpiperidinium benzenesulphinate (**3a**)*: mp 169-170 °C; ^1H NMR δ = 1.44 (12H, s), 1.58 (6H, br-s), 7.39 (3H, m), 7.73 (2H, m). Anal. Calcd for $C_{15}H_{25}NO_2S$: C, 63.57; H, 8.90; N, 4.95; S, 11.29. Found: C, 63.34; H, 8.91; N, 4.90; S, 11.34.

*2,2,6,6-Tetramethylpiperidinium p-toluenesulphinate (**3b**)*: mp 215-216 °C; ^1H NMR δ = 1.44 (12H, s), 1.59 (6H, s), 2.35 (3H, s), 7.19 (2H, d, J = 8.7 Hz), 7.60 (2H, d, J = 8.7 Hz). Anal. Calcd. for $C_{16}H_{27}NO_2S$: C, 64.61; H, 9.17; N, 4.95; S, 10.76. Found: C, 64.55; H, 9.15; N, 4.97; S, 10.72.

*Synthesis of tetramethylpiperidinium benzenesulphonates **4a** and **4b***

A solution of tetramethylpiperidine (0.42 g, 3 mmol) in 5 ml CH_3CN and a solution of the appropriate benzenesulphonic acid (3 mmol) dissolved in 10 ml of CH_3CN were mixed together under magnetic stirring. The salts **4a** and **4b**, precipitated from the reaction mixture in quantitative yield, were filtered and purified by crystallization from CH_3CN.

*2,2,6,6-Tetramethylpiperidinium benzenesulphonate (**4a**)*: mp 170-171 °C; ^1H NMR δ = 1.48 (12H, s), 1.63 (6H, s), 7.39 (3H, m), 7.89 (2H, m). Anal. Calcd. for $C_{15}H_{25}NO_3S$: C, 60.17; H, 8.42; N, 4.68; S, 10.69. Found: C, 60.30; H, 8.44; N, 4.66; S, 10.70.

*2,2,6,6-Tetramethylpiperidinium p-toluenesulphonate (**4b**)*: mp 119-120 °C; ^1H NMR δ = 1.48 (12H, s), 1.64 (6H, s), 2.37 (3H, s), 7.20 (2H, d, J = 8.6 Hz), 7.78 (2H, d, J = 8.6 Hz). Anal. Calcd. for $C_{16}H_{27}NO_3S$: C, 61.31; H, 8.69; N, 4.47; S, 10.21. Found: C, 61.36; H, 8.70; N, 4.45; S, 10.23.

*Synthesis of S-(p-tert-butylphenyl)-p-tert-butylbenzenethiosulphonate (**7c**)*

This compound was prepared following the method reported in the literature[9]. *m*-Chloroperbenzoic acid (0.093 g, 0.54 mmol) was added under magnetic stirring to a solution of aryldisulphide **5c** (0.05 g, 0.15 mmol) in 5 ml benzene, and the reaction was left to react overnight. The reaction was then concentrated under reduced pressure, taken up with $CHCl_3$ and chromatographed on preparative silica-gel plates eluting with cyclohexane/ethyl acetate 9:1. Compound **7c** corresponding to the uppermost spot was obtained in 30 mg yield: mp 143-145 °C from ethyl acetate; ^1H NMR δ = 1.32 (9H, s), 1.33 (9H, s), 7.28 (2H, d, J = 8.6 Hz),

7.34 (2H, d, J = 8.6 Hz), 7.40 (2H, d, J = 8.6 Hz), 7.49 (2H, d, J = 8.6 Hz); IR ν_{max} 1585, 1320, 1140, 1100 cm^{-1}; MS *m/z* (rel int) 362 (M^+, 18) 181 (100). Anal. Calcd. for $C_{20}H_{26}O_2S_2$: C, 66.27; H, 7.24; S, 17.66. Found: C, 66.31; H, 7.25; S, 17.68.

Table 3. Experimental Data for the X-ray Diffraction Studies on Crystalline Compounds 8c and 9b.

Compound	8b	9c
formula	$C_{16}H_{25}NOS$	$C_{19}H_{31}NO_2S$
cryst habit	prisms	flattened prisms
cryst colour	colourless	colourless
M_w	279.4	337.5
F(000)	608	1472
cryst syst	monoclinic	orthorhombic
space group	P 2_1/n	P c a 2_1
cell parameters at 295 K[a]		
a Å	21.100(4)	25.139(4)
b Å	8.215(2)	6.437(2)
c Å	9.276(2)	23.669(4)
α deg	90	90
β deg	90.8(1)	90
γ deg	90	90
V $Å^3$	1607.7(6)	3830(15)
Z	4	8
D_c g cm^{-3}	1.15	1.17
crystal dim mm	0.14x0.19x0.24	0.09x0.14x0.29
μ cm^{-1}	17.2	15.6
diffractometer	Siemens AED	Siemens AED
scan type	ω-2ϑ	ω-2ϑ
scan width deg	b	b
radiation	c	c
ϑ range collcn deg	3-70	3-70
unique total data	3043	3720
criterion of obsn	I>2σ(I)	I>2σ(I)
unique obsd data	2374	1751
no. of refined par	272	322
absorption	d	d
solution	e	e
H atoms	f	f
R	0.049	0.051
R_w	0.054	0.049
largest shift/esd	0.02	0.02
largest peak $eÅ^{-3}$	0.14	0.11
computer and programs	g	g

a: unit cell parameters were obtained by least-squares analysis of the setting angles of 30 carefully centered reflections chosen from diverse region of reciprocal space; b: from (ϑ-0.6) to [ϑ+(0.6+Δϑ)]° where $\Delta\vartheta = [(\lambda\alpha_2-\lambda\alpha_1)/\lambda]\tan\vartheta$; c: Ni-filtered Cu-Kα (λ = 1.54178 Å); d: no correction applied; e: direct methods; f: located in ΔF map and isotropically refined; g: ENCORE E91, SHELXS86,[22] SHELX76,[23] PARST[24].
$R = \Sigma\,|\Delta F|/\Sigma\,|F_o|$; $Rw = [\Sigma w(\Delta F^2)^2/\Sigma w(F_o^2)^2]$

Light induced decomposition of p-toluenesulphonyl chloride in the presence of TEMPO.

TEMPO (0.624 g, 4 mmol) and *p*-toluenesulphonyl chloride (0.95 g, 5 mmol) were dissolved in 30 ml benzene and 1 ml MeOH and irradiated for 3 hrs. The reaction was then concentrated and taken up with 50 ml

of CH_3CN/Et_2O 3:7. From the reaction, 0.600 g of a mixture of tetramethylpiperidinium chloride (characterized by comparison of its ^1H NMR and IR spectra with an authentic sample synthesized by bubbling $HCl_{(g)}$ in a solution of tetramethylpiperidine in benzene) and sulphonate **4b** were isolated in the ratio 1.5:1 respectively.

Crystallographic Section

Experimental data for the X-ray diffraction studies on crystalline compounds **8b** and **9c** are reported in Table 3.

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