61.9, 62.2, 71.0, 71.2; MS, *m/e* 290 (M^+). Anal. Calcd for $C_{14}H_{27}O_4P$: C, 57.92; H, 9.37; P, 10.67. Found: C, 58.05; H, 9.52; P, 10.58.

2c: IR (neat) 3640–3160, 1220, 1020, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–2.2 (m, 13 H), 2.2–3.4 (m, 3 H), 3.9–4.4 (quintet, 4 H, J = 7.2 Hz), 7.0–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.8, 12.6, 12.8, 15.7, 16.1, 22.5, 26.8, 26.9, 28.8, 28.9, 30.5, 61.3, 61.5, 61.7, 62.0, 73.5, 73.7, 125.6, 126.5, 127.7, 135.1, 135.2; MS, *m/e* 312 (M^+). Anal. Calcd for $C_{16}H_{25}O_4P$: C, 61.53; H, 8.07; P, 9.92. Found: C, 61.37; H, 8.33; P, 10.02.

3a: IR (neat) 3600–3120, 1220, 1020, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–2.1, (m, 22 H), 3.3–4.7 (m, 6 H), 7.1–7.6 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.8, 15.7, 16.0, 21.8, 22.4, 22.6, 22.8, 22.9, 27.9, 28.0, 28.9, 29.4, 29.8, 30.5, 31.6, 61.1, 61.2, 61.5, 61.8, 73.4, 73.5, 125.8, 126.6, 127.5, 143.0, 143.1; MS, *m/e* 368 (M^+). Anal. Calcd for $C_{20}H_{33}O_4P$: C, 65.20; H, 9.03; P, 8.41. Found: C, 65.11; H, 8.95; P, 8.32.

3b: IR (neat) 3680–3100, 1200, 1020, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9–2.5 (m, 16 H), 3.1–5.3 (m, 6 H), 7.1–7.7 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 15.9, 16.2, 18.2, 18.3, 18.8, 19.0, 19.2, 19.4, 20.4, 20.6, 21.9, 25.1, 33.1, 61.3, 61.5, 61.6, 61.8, 69.8, 70.0, 126.3, 126.6, 127.7, 142.8; MS, *m/e* 338 (M^+). Anal. Calcd for $C_{18}H_{27}O_4P$: C, 63.89; H, 8.05; P, 9.15. Found: C, 64.09; H, 8.08; P, 9.30.

3c: IR (neat) 3540–3140, 1230, 1020, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9–1.8 (m, 8 H), 2.6–3.2 (m, 1 H), 3.4–4.3 (m, 6 H), 7.0–7.6 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 13.6, 13.7, 15.5, 15.8, 24.0, 27.1, 32.1, 61.2, 61.5, 72.3, 72.4, 125.7, 126.4, 126.6, 127.1, 127.7, 129.2, 134.9, 135.0, 142.6; MS, *m/e* 360 (M^+). Anal. Calcd for $C_{20}H_{25}O_4P$: C, 66.66; H, 6.99; P, 8.60. Found: C, 66.45; H, 6.76; P, 8.91.

4b: IR (neat) 3620–3080, 1210, 1020, 960, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1–2.3 (m, 16 H), 3.8–4.6 (m, 6 H), 6.43 (dd, 1 H, J = 16.0, 4.0 Hz), 6.73 (d, 1 H, J = 16.0 Hz), 7.1–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 16.1, 16.4, 17.4, 17.5, 17.9, 18.1, 18.3, 18.7, 18.8, 21.6, 21.7, 21.9, 22.0, 23.2, 31.1, 61.7, 62.0, 62.3, 69.2, 69.3, 126.3, 127.2, 128.4, 129.1, 131.1, 131.2, 137.1; MS, *m/e* 364 (M^+). Anal. Calcd for $C_{20}H_{29}O_4P$: C, 65.92; H, 8.02; P, 8.50. Found: C, 65.88; H, 7.93; P, 8.65.

5b: IR (neat) 3620–3160, 1230, 1020, 960, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9–2.0 (m, 19 H), 3.7–4.4 (m, 6 H), 5.5–6.0 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.0, 16.2, 17.1, 17.4, 17.7, 17.8, 18.2, 18.4, 21.6, 22.6, 30.5, 61.3, 61.6, 61.9, 69.0, 69.2, 125.0, 132.4; MS, *m/e* 302 (M^+). Anal. Calcd for $C_{15}H_{27}O_4P$: C, 59.59; H, 9.00; P, 10.25. Found: C, 59.82; H, 8.82; P, 10.37.

Isomerization of *endo*-1b. The endo phosphonate **1b** (0.116 g, 0.5 mmol) was treated with lithium diisopropylamide (0.75 mmol) in THF at −78 °C for 1 h as mentioned above and then worked up with dilute HCl (aq) at the same temperature. After the extraction with ether (3 × 10 mL), the combined organic layers were washed with saturated $NaHCO_3$ solution and dried ($MgSO_4$). Evaporation gave *exo*-**1b** (98% conversion).

Preparation of 7-Benzylidenenorcarane (6). To a suspension of NaH (0.93 mmol, washed with *n*-hexane) in THF (10 mL) was added **3b** (0.242 g, 0.715 mmol) in THF (5 mL) dropwise at room temperature. Then, a catalytic amount of 18-crown-6 was added to the reaction mixture which was stirred for 5 h at reflux. The mixture was poured into water (5 mL), which was extracted with ether (3 × 30 mL). The combined organic layers were washed with saturated $NaHSO_4$ solution and brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on a silica gel column to give **6** in 53% yield.

Preparation of 1,4-Diphenyl-1,3-butadiene (7). The reaction of **3c** was carried out similarly as mentioned above to give **7** in 31% yield.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Developmental Scientific Research from the Ministry of Education, Science, and Culture.

Registry No. *cis*-**1a**, 89352-07-8; *trans*-**1a**, 89352-11-4; *endo*-**1b**, 89352-12-5; *exo*-**1b**, 89352-08-9; *cis*-**1c**, 89352-09-0; *trans*-**1c**, 89352-13-6; *cis*-**2a**, 99327-86-3; *trans*-**2a**, 99327-85-2; **2b**, 99342-36-6; **2c**, 99327-92-1; *cis*-**3a**, 99327-87-4; *trans*-**3a**, 99327-88-5; **3b**, 99327-89-6; **3c**, 99327-93-2; **4b**, 99327-90-9; **5b**, 99327-91-0; **6**, 82253-12-1; **7**, 886-65-7; LDA, 4111-54-0; EtCHO, 123-38-6; PhCHO, 100-52-7; (*E*)-3-phenyl-2-pentenal, 14371-10-9; (*E*)-2-butenal, 123-73-9.

Electron Spin Resonance Spectroscopic Study of New Persistent Nitrogen-Centered Free Radicals: *N*-(Arylthio)-4-toluenesulfonamidyls[1]

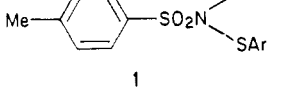
Yozo Miura,* Teruo Kunishi, and Masayoshi Kinoshita

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

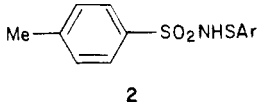
Received May 29, 1985

In contrast to a number of the electron spin resonance (ESR) spectroscopic studies of sulfonamidyl ($RSO_2\dot{N}R'$)[2] and *N*-alkoxysulfonamidyl radicals ($RSO_2\dot{N}OR'$),[3-5] there has appeared no ESR study of *N*-thiosulfonamidyl radicals ($RSO_2\dot{N}SR'$) in the literature.[6] We have recently studied a variety of *N*-(alkylthio)- and *N*-(arylthio)aminyl radicals ($R\dot{N}SR'$) by ESR spectroscopy.[1] These radicals are essentially fairly long-lived in solution since they are significantly stabilized by the conjugative electron delocalization from the nitrogen to the sulfur ($-\dot{N}-\ddot{S}- \leftrightarrow -\ddot{N}^- - \dot{S}^+-$), and some sterically protected *N*-thioaminyl radicals can be isolated as radical crystals[8] or hydrazine dimers.[9] To continue our interest in ESR studies on *N*-thioaminyl radicals, we dealt with *N*-thiosulfonamidyl radicals. In the radicals a donor (sulfenyl) and an acceptor (sulfonyl) group are both attached directly to the radical center, and for such a structure of radical captodative radical stabilization substituent effects might be expected.[10,11] In this paper we report the first ESR study of *N*-thiosulfonamidyl radicals.

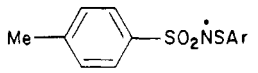
The *N*-thiosulfonamidyl radicals treated in this work are *N*-(arylthio)-4-toluenesulfonamidyls (**3**), which have been



1



2



3

a, Ar = Ph **c**, Ar = 4-MeC_6H_4 **e**, Ar = 4-ClC_6H_4
b, Ar = C_6D_5 **d**, Ar = 4-$MeOC_6H_4$ **f**, Ar = 4-$NO_2C_6H_4$

(1) ESR Studies of Nitrogen-Centered Free Radicals. 26. Part 25: Miura, Y.; Kunishi, T.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1696.

(2) (a) Zomer, G.; Engberts, J. B. F. N. *Tetrahedron Lett.* **1977**, *3901*. (b) Miura, Y.; Nakamura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 947. (c) Danen, W. C.; Gellert, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 3264. (d) Sutcliffe, R.; Anpo, M.; Stolow, A.; Ingold, K. U. *J. Am. Chem. Soc.* **1982**, *104*, 6064. (e) Teeninga, H.; Engberts, J. B. F. N. *J. Org. Chem.* **1983**, *48*, 537.

(3) Teeninga, H.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays*-Bas **1978**, *97*, 59.

(4) Teeninga, H.; Zomer, B.; Engberts, J. B. F. N. *J. Org. Chem.* **1979**, *44*, 4717.

(5) Forrester, A. R.; Johansson, E. M.; Thomson, R. H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1112.

(6) A strong ESR signal made of a 1:1:1 triplet was observed during the course of the reaction of *S,S*-diphenyl-*N*-(4-toluenesulfonyl)sulfilimine with diphenyl disulfide or of the thermolysis of **1a**, and this was tentatively identified as **3a**. However, the ESR parameters for the radical have never been reported.[7]

(7) Oae, S.; Tsuchida, Y.; Tsujihara, K.; Furukawa, N. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2856.

(8) Miura, Y.; Yamamoto, A.; Katsura, Y.; Kinoshita, M. *J. Org. Chem.* **1980**, *45*, 3875.

(9) Miura, Y.; Yamamoto, A.; Katsura, Y.; Kinoshita, M.; Sato, S.; Tamura, C. *J. Org. Chem.* **1982**, *47*, 2618.

(10) Viehe, H. G.; Merényi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917.

(11) Since, however, sulfonyl groups have little or no ability to delocalize the unpaired electron as mentioned below, the present case may not belong to the category of the true captodative substituent effects.

0022-3263/85/1950-5862$01.50/0

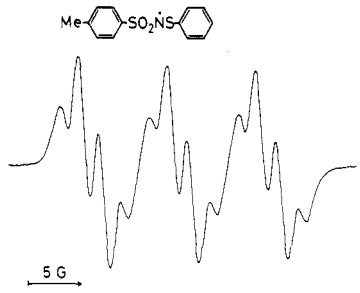


Figure 1. ESR spectrum of **3a** recorded during photolysis of a solution of **1a** in benzene at 15 °C.

Table I. ESR Parameters for *N*-(Arylthio)-4-toluenesulfonamidyl Radicals (3)[a,b]

	a_N	a_H[c,d]	a^{33}_S	g	method[e]
3a	8.47	1.82 (3)		2.0074	a
3a	8.50	1.84 (3)		2.0074	b
3b	8.45		11.9	2.0074	a
3c	8.27[f]	1.9 (2)[f]	12.0	2.0074	a
3c	8.25[f]	1.9 (2)[f]		2.0074	b
3d	7.90	1.81 (2)	12.3	2.0074	a
3e	8.51	1.8 (2)		2.0075	a
3e	8.50	1.8 (2)		2.0075	b
3f	8.94	1.8 (2)		2.0073	b

[a] In benzene at 15 °C. [b] Hyperfine splitting constants are given in Gauss. [c] Values for aromatic protons of the phenylthio benzene ring. [d] Numbers in parentheses refer to the number of equivalent protons. [e] Method of generation of radicals (see text). [f] a_H^{Me} (Me at the phenylthio benzene ring) = 2.1 G.

generated in benzene by either or both of the following two methods: (a) photolysis of *N,N*-bis(arylthio)-4-toluenesulfonamides (**1**)[7] with a high-pressure mercury or a xenon lamp and (b) oxidation of *N*-(arylthio)-4-toluenesulfonamides (**2**)[12] with lead dioxide. Both methods gave relatively clean ESR spectra, and more intense spectra were provided by method a. Typical ESR spectra are illustrated in Figures 1 and 2, and their ESR parameters are listed in Table I.

All the ESR spectra of **3** are split into an 1:1:1 triplet by the interaction with the central nitrogen, and each component of the triplet is further split by the interaction with protons in the arylthiyl group. For instance, the spectrum of **3a** is split into 1:3:3:1 quartets of an 1:1:1 triplet, as found in Figure 1. It is obvious that the quartet splittings are attributable to the interaction with the three magnetically almost equivalent ortho and para protons of the phenylthio benzene ring; this assignment is further confirmed by the ESR spectrum of **3b** with a deuterated phenylthiyl group, which is constituted of a simple 1:1:1 triplet. On the other hand, no splittings to any protons in the tosyl groups were found.

Interstingly, sulfur-33 hyferfine splittings were observed in the wings of the spectra of **3b–d** on recording at high gain when high-concentration solutions of **1** were irradiated with a high-power xenon lamp (1 kW). As found in Figure 2, the $M_N = +1$, $M_S = +^3/_2$ and $M_N = -1$, $M_S = -^3/_2$ groups are completely resolved, while the $M_N = 0$, $M_S = +^3/_2$ and $M_N = 0$, $M_N = -^3/_2$ groups are lost partly in the envelope of the main spectrum, and the other groups are completely lost. The measured intensitites of the satellite lines corresponds to 0.21% of the parent spectrum. This value agrees with the theoretical intensity ratio of 0.19% estimated from the natural abundance (0.76%) of sulfur-33.

From the ESR results summarized in Table I, it can be safely concluded that in **3** the unpaired electron resides

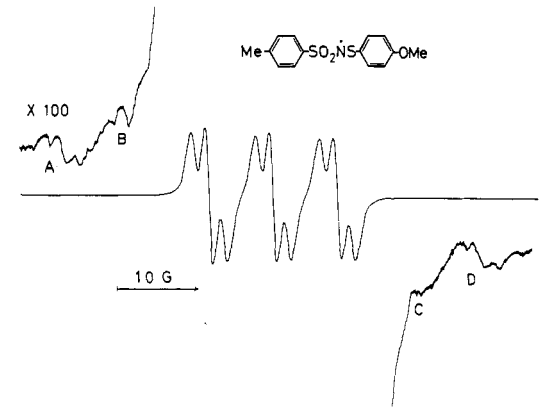
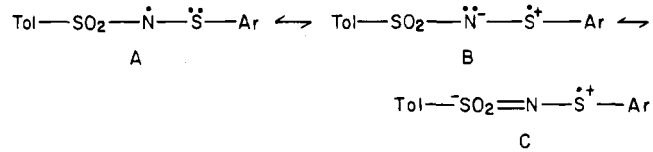


Figure 2. ESR spectrum of **3d** recorded during photolysis of a solution of **1d** in benzene at 15 °C. The wings are shown at high gain (100 times), and satellite lines due to ^{33}S atom are clearly seen; assignments of the satellite lines are given as follows (assuming that a_N and a^{33}_S both are positive): (A) $M_N = +1$, $M_S = +^3/_2$; (B) $M_N = 0$, $M_S = +^3/_2$; (C) $M_N = 0$, $M_S = -^3/_2$; (D) $M_N = -1$, $M_S = +^3/_2$.

mainly on the (central) nitrogen and the divalent sulfur, and there is little or no delocalization of the unpaired electron over the tosyl groups. The same conclusion has been drawn previously for sulfonylcarbinyl[13] and sulfonamidly radicals.[2] Accordingly, radicals **3** can be best represented by the three principal canonical structures A–C. It is obvious that this substantial spin density on the divalent sulfur (which is sufficient to induce a spin–orbit coupling effect)[14] increases largely the g values of **3**.[15]



As found in Table I, when radicals **3** have an electron-donating substituent at the phenylthio benzene ring, the a_N values are further reduced and the a^{33}_S values are further increased. Similar substituent effects have often been observed for the radicals of –Ċ–Ẍ– and –Ṅ–Ẍ– structures, including nitroxides.[17] We account for these substituent effects in terms of a further enhancement of the relative importance of canonical structures B and C by electron-donating substituents.

It is of interest to compare the ESR parameters for **3** with structurally related radicals such as RṄSAr[18] and ArCOṄSAr.[19] When the a_N and a^{33}_S values for **3** are compared with those (a_N 11.6–12.26 G, a^{33}_S = 5.75–6.7 G) for RṄSAr radicals, we find that the a_N values are ca. 3.4 G lower than those for the latter radicals and the a^{33}_S values are indeed ca. 6.2 G increased from those for the latter radicals. These remarkable reduction in a_N and remarkable increase in a^{33}_S can be accounted for both by a substantial increase in the relative importance of dipolar canonical structure B and by an additional contribution of dipolar canonical structure C.

(12) Oae, S.; Tsujihara, K.; Furukawa, N. *Tetrahedron Lett.* **1970**, 2663.

(13) Carton, P. M.; Gilbert, B. C.; Laue, H. A. H.; Norman, R. O. C.; Sealy, R. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1245.

(14) The sulfur spin–orbit coupling parameter has been reported to be 382 cm^{-1}: McClure, D. S. *J. Chem. Phys.* **1949**, *17*, 905.

(15) The g values for typical nitrogen-centered free radicals lie in the range 2.003–2.005.[16]

(16) Danen, W. C.; Neugebauer, F. A. *Angw. Chem., Int. Ed. Engl.* **1975**, *14*, 783.

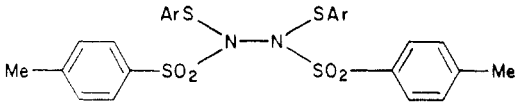
(17) For instance, see: Miura, Y.; Kunishi, T.; Isogai, M.; Kinoshita M. *J. Org. Chem.* **1975**, *50*, 1627.

(18) Miura, Y.; Kinoshita, M. *J. Org. Chem.* **1984**, *49*, 2724.

(19) Miura, Y.; Katsura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3004.

Furthermore, we note the a_N values (6.80–7.38 G) for ArCONSAr′ radicals are ca. 1.3 G lower than those for **3**. It is obvious that this reduction in a_N found in going from **3** to ArCONSAr′ radicals is partly attributable to some delocalization of the unpaired electron onto the carbonyl group in ArCONSAr′ radicals.[20]

In contrast to the well-known transient properties of sulfonamidyl radicals,[2,21] radicals **3** persist in solution over a long period ($\tau_{1/2}$ > 5 h in benzene at 15 °C), and degassing of the ESR samples had no effect other than to sharpen the ESR lines. Accordingly, it could be readily shown, by raising and lowering the temperature, that the radicals exist in equilibrium with a diamagnetic dimer. The enthalpies of dissociation ($\Delta H°$) for the dimers of **3**, measured in benzene by the method of Vinco et al.,[22,23] were 15.9 ± 0.8 (for the dimer of **3a**) and 16.1 ± 0.5 kcal/mol (for the dimer of **3e**).[24] We assume that the structures of the dimers are hydrazine type **4** and that such

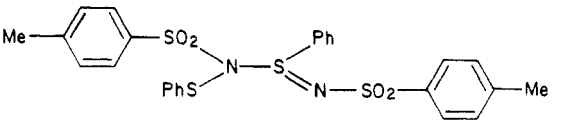


4

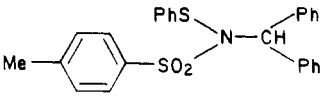
lower $\Delta H°$ values[26] result principally from the electronic stabilization in **3**, which would weaken the N–N bonds, by the captodative substituent effects.[10] In addition, steric crowding around the N–N bonds in **4** may further weaken the N–N bonds since the formation of the, probably shorter, N–N bonds that would be induced by strong electron-withdrawing properties of sulfonyl groups, may be prevented by the steric crowding.[27]

Interestingly, a solution of sulfilimine **5**[28] also yielded an ESR spectrum attributable to **3a**; its identification was made by its ESR parameters: a_N = 8.44 (1 N), a_H = 1.81 (3 H), g = 2.0074 (in benzene). As shown by its structure, **5** is isomeric with dimers **4**. From this and its ESR observation, we considered the possibility that **5** and its substituted sulfilimines were the corresponding dimers of **3**. However, we could rule out this possibility because the ESR signal was very weak.

However, when a solution of **5** in 1:2 (v/v) dichloromethane–benzene was heated to 45 °C, the ESR signal gradually developed with time, this observation strongly suggesting that **3a** was generated via thermolysis of **5**. In order to examine the products derived from the thermolysis, **5** was heated in benzene at 60 °C for 8 h. The products isolated are **1a** (24%) and small amounts of diphenyl disulfide. It is obvious that **1a** is derived from the radical-coupling reaction between one molecule of **3a** and a phenylthiyl radical. Furthermore, when **5** was heated in dichloromethane at 50 °C for 5 h in the presence of azobis(diphenylmethane), **6** was isolated in 12% yield from the reaction mixture. These reactions clearly indicate that **5**, on thermolysis, gives **3a** and this thermolysis may be one of the good methods for generation of **3**.



5



6

Experimental Section

^{1}H NMR spectra were recorded with a JEOL JNM PS-100 spectrometer and chemical shifts (δ) are expressed relative to internal tetramethylsilane. IR spectra were obtained with a Jasco A-200 spectrophotometer and UV spectra with a Shimadzu UV-240 spectrophotometer. ESR spectra were measured with a JEOL JES-ME-3X or JEOL JES-FE-2XG (Tokushima) spectrometer equipped with an X-band microwave unit and 100-kHz field modulation. Hyperfine splitting constants were measured to within ±0.1 (for a_N and a_H) or ±0.2 G (for $a_{^{33}S}$) and g values to ±0.0002 by comparison with Fremy's salt in K_2CO_3 aqueous solution (a_N = 13.09 G,[29] g = 2.0057[30]).

Diaryl disulfides were prepared from the corresponding benzenethiols by iodine oxidation. Azobis(diphenylmethane)[25,26] [mp 114–116 °C (lit.[31] mp 115 °C)], sulfilimine **5**[28] [mp 118–120 °C (lit.[28] mp 121–124 °C)], and *S*-aryl-*S*-ethyl-*N*-(4-toluenesulfonyl)sulfilimines[34] were obtained by the reported methods, respectively.

N,*N*-Bis(arylthio)-4-toluenesulfonamides (**1**) were prepared according to the reported procedure.[7] However, the solvent used was *o*-dichlorobenzene in most cases. In a general procedure, a solution of *S*,*S*-diphenyl-*N*-(4-toluenesulfonyl)sulfilimine (360 mg, 1.0 mmol) and diaryl disulfide (1.0 mmol) in 2.5 mL of chloro (for **1d**) or *o*-dichlorobenzene (for **1a–c,e**) was heated at 120–165 °C until the solution turned orange or red. The reaction mixture was then column chromatographed on silica gel (Wako gel C-200, column size 3 × 10 cm).[35] Elution with 1:1 (v/v) benzene–hexane gave a mixture of diaryl disulfide and diphenyl sulfide, and subsequent elution with benzene gave **1**, which was crystallized from methanol. In the case of **1d**, however, the reaction mixture was eluted with benzene from the first.

***N*,*N*-Bis(phenylthio)-4-toluenesulfonamide (1a).** On heating at 150 °C for ~30 min, the reaction mixture, after chromatography and subsequent crystallization, gave 66 mg (17%) of **1a**: mp 94–95 °C (lit.[7] mp 97.5–98 °C); UV (benzene) λ_{max} 313 nm (ϵ 2140), 277 (4670).

***N*,*N*-Bis(phenyl-*d*$_5$-thio)-4-toluenesulfonamide (1b).** On heating at 150 °C for ~50 min, the reaction mixture, after

(20) Although, in a previous paper,[19] we assumed that the extent of delocalization of the unpaired electron onto the carbonyl group in ArCONSAr′ radicals was negligibly small, our recent ESR studies on an ^{17}O-enriched (ca. 7%) PhCONSPh radical showed $a_{^{17}O}$ = 2.22 G (unpublissed results). This magnitude of $a_{^{17}O}$ indicates some delocalization of the unpaired electron onto the carbonyl group.

(21) For *N*-alkoxysulfonamidyl radicals, the half-lives of a few seconds (at −50 °C) were reported. See Reference 3.

(22) Vincoa, G.; Dauben, H. J., Jr.; Hunter, F. R.; Volland, W. V. *J. Am. Chem. Soc.* **1969**, *91*, 2823.

(23) According to the method, the $\Delta H°$ values are calculated from a plot of ln (cT) *vs.* $1/T$, where c is the relative radical concentration and T is the absolute temperature. In this work the relative radical concentrations were measured from the areas under the absorption curves of the singly integrated ESR spectra that were obtained on a JEOL JES-ID-2 integrator. Measurements were carried out at four different temperatures between 5 and 35 °C, and the temperaturs of the ESR cavity were measured with a copper-constantan thermocouple.

(24) The $\Delta H°$ measurements were repeated at least four times for each radical and averaged. Errors are standard deviations.

(25) Although some attempts were made to isolate the dimers (e.g., photolysis of **1** or oxidation of **2** with inorganic oxidizing agents), these procedures were all unsuccessful.

(26) Compare, for example, the values (20.2–21.2 kcal/mol) for the dimers made of RNSAr radicals.[15]

(27) Schlosser, K.; Steenken, S. *J. Am. Chem. Soc.* **1983**, *105*, 1504.

(28) Barton, D. H. R.; Kelly, M. R.; Ferreira, D. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1090 (or 1682).

(29) Faber, R. J.; Fraenkel, G. K. *J. Chem. Phys.* **1967**, *47*, 2462.

(30) Wertz, J. E.; Reitz, D. C.; Dravnieks, F. "Free Radicals in Biological Systems"; Blois, M. S., Jr., et al., Eds.; Academic Press: New York, 1961; p 186.

(31) Cohen, S. G.; Wang, C. H. *J. Am. Chem. Soc.* **1955**, *77*, 2457.

(32) Benzophenone azine was obtained in 33% yield by heating a mixture of 20 g (0.11 mol) of benzophenone and 11.2 g (0.22 mol) of 50% hydrazine hydrate in 30 mL of acetic acid for 1 h under reflux.[33]

(33) Kambara, S.; Joh, S. "Yuki Kagobutsu Goseiho"; Gihodo: Tokyo, 1955; Vol. 7, p 41.

(34) Tsujihara, K.; Furukawa, N.; Oae, K.; Oae, S. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2631.

(35) It is likely that during the column chromatography products **1** are in part decomposed to give diaryl disulfide as one of the decomposition products.

chromatography and subsequent crystallization, gave **1b** as colorless needles: mp 90–92 °C; 17% yield (69 mg); UV (benzene) λ_{max} 313 nm (ϵ 2240), 277 (4700); ^{1}H NMR ($CDCl_3$) δ 2.36 (s, Me, 3 H), 7.18 and 7.72 (each d, J = 8.2 Hz, aromatic, 4 H). Anal. Calcd for $C_{19}H_7D_{10}NO_2S_3$: C, 57.39; H, 4.31; N, 3.52. Found: C, 57.53; H, 4.45; N, 3.36.

***N,N*-Bis(4-tolylthio)-4-toluenesulfonamide (1c).** On heating at 150 °C for ~20 min, the reaction mixture, after chromatography and subsequent crystallization, gave 120 mg (29%) of **1c**: mp 94.5–95.5 °C (lit.[7] mp 94.5 °C); UV (benzene) λ_{max} 316 nm (ϵ 2760), 277 (5810).

***N,N*-Bis[(4-methoxyphenyl)thio]-4-toluenesulfonamide (1d).** On heating at 120 °C for 10 min, the reaction mixture, after chromatography and subsequent crystallization, gave 61 mg (14%) of **1d**: mp 90–91 °C (lit.[7] mp 92.5 °C); UV (benzene) λ_{max} 315 nm (sh) (ϵ 3840), 277 (12 200).

***N,N*-Bis[(4-chlorophenyl)thio]-4-toluenesulfonamide (1e).** On heating at 165 °C for ~1 h, the reaction mixture, after chromatography and subsequent crystallization, gave 58 mg (13%) of **1e**: mp 111–112 °C (lit.[7] mp 111–112 °C); UV (benzene) λ_{max} 315 nm (ϵ 2800), 277 (6600).

N-(Arylthio)-4-toluenesulfonamides (**2**) were prepared by heating a solution of *S*-aryl-*S*-ethyl-*N*-(4-toluenesulfonyl)sulfilimines (0.65 mmol) in refluxing toluene (4 mL) for 1–2 h according to the reported procedure and were purified by repeated recrystallization from benzene–hexane.[12]

***N*-(Phenylthio)-4-toluenesulfonamide (2a)**: colorless needles; mp 97–99 °C (lit.[12] mp 113–115 °C); yield 97 mg (53%); IR (KBr) 3230 (NH), 1290 and 1160 cm^{-1} (SO_2); ^{1}H NMR ($CDCl_3$) δ 2.36 (s, Me, 3 H), 6.55 (s, NH, 1 H), 7.12–7.79 (m, aromatic, 9 H).

***N*-(4-Tolylthio)-4-toluenesulfonamide (2c)**:[36] colorless needles; mp 101–103 °C; yield 79 mg (41%); IR (KBr) 3210 (NH), 1290 and 1160 cm^{-1} (SO_2); ^{1}H NMR ($CDCl_3$) δ 2.25 (s, Me, 3 H), 2.33 (s, Me, 3 H), 6.74 (s, NH, 1 H), 6.93 –7.77 (m, aromatic, 8 H).

***N*-[(4-Chlorophenyl)thio]-4-toluenesulfonamide (2e)**: colorless prisms; mp 107–109 °C; yield 135 mg (65%); IR (KBr) 3200 (NH), 1320 and 1160 cm^{-1} (SO_2); ^{1}H NMR ($CDCl_3$) δ 2.35 (s, Me, 3 H), 6.96 (s, NH, 1 H), 7.06–7.76 (m, aromatic, 8 H). Anal. Calcd for $C_{13}H_{12}ClNO_2S_2$: C, 49.75; H, 3.85; N, 4.46. Found: C, 50.14; H, 3.79; N, 4.20.

***N*-[(4-Nitrophenyl)thio]-4-toluenesulfonamide (1f)**:[36] light brown prisms; mp 142–143 °C; yield 104 mg (49%); IR (KBr) 3200 (NH), 1340 and 1160 cm^{-1} (SO_2); ^{1}H NMR ($CDCl_3$) δ 2.38 (s, Me, 3 H), 6.62 (s, NH, 1 H), 7.18–8.09 (m, aromatic, 8 H).

Thermolysis of 5. In a glass tube were placed **5** (300 mg, 0.537 mmol) and benzene (10 mL), and the mixture was degassed by three freeze–pump–thaw cycles. After the tube was sealed off from the vacuum system, the mixture was heated to 60 °C for 8 h. After concentration, the residue was column chromatographed on silica gel (Wako gel C-200, column size 3 × 10 cm). Elution with 1:1 (v/v) benzene–hexane gave diphenyl disulfide, and subsequent elution with benzene gave **1a** (82 mg, 39%) containing small amounts of impurities that on crystallization from methanol, afforded colorless needles: mp 94–95 °C (lit.[7] mp 97.5–98 °C); 24% yield (50 mg, 0.13 mmol). The IR and ^{1}H NMR spectra were in complete agreement with those of an authentic sample.

Reaction of 5 with Azobis(diphenylmethane). In a glass tube were placed **5** (200 mg, 0.36 mmol), azobis(diphenylmethane) (390 mg, 1.1 mmol), and dichloromethane (10 mL). After the mixture was degassed as above, the tube was sealed off and the mixture was heated to 50 °C for 5 h. After concentration, the residue was column chromatographed on silica gel (Wako gel C-200, column size 3 × 20 cm) with benzene as eluant to give a semisolid mass (100 mg) that on crystallization from hexane, afforded colorless prisms: mp 121–123 °C; 12% yield (37 mg, 0.083 mmol); ^{1}H NMR ($CDCl_3$) δ 2.34 (s, Me, 3 H), 6.76 (s, Ph_2CH, 1 H), 6.70–7.63 (m, aromatic, 19 H); mass spectrum (35 eV), *m/e* 218 (21), 182 (71), 181 (23), 180 (27), 168 (63), 167 (100), 109 (44), 91 (39). Anal. Calcd for $C_{26}H_{23}NO_2S_2$: C, 70.08; H, 5.20; N, 3.14. Found: C, 70.31; H, 5.42; N, 3.01.

Generation of Radicals. Radicals **3** were generated in benzene by either or both of the following two methods: (a) photolysis of a solution of **1** with an 100-W high-pressure mercury or an 1-kW xenon lamp and (b) oxidation of a solution of **2** with PbO_2. All ESR samples were degassed by three freeze–pump–thaw cycles using a high-vacuum line.

Acknowledgment. The authors thank Professor T. Ohta and Dr. H. Tanaka of Tokushima University for the use of an ESR instrument and valuable suggestions on the ESR data. They also thank Professor N. Furukawa of Tsukuba University for valuable suggestions and discussion on the syntheses of sulfilimines and related compounds.

Registry No. **1a**, 37753-02-9; **1b**, 99397-59-8; **1c**, 37753-03-0; **1d**, 37753-04-1; **1e**, 37753-05-2; **1f**, 99376-69-9; **2a**, 29723-57-7; **2c**, 99376-70-2; **2e**, 99376-71-3; **3a**, 99376-73-5; **3b**, 99376-74-6; **3c**, 99376-75-7; **3d**, 99376-76-8; **3e**, 99376-77-9; **3f**, 99376-78-0; **5**, 28833-59-2; **6**, 99376-72-4; TsN=SPh_2, 13150-76-0; Ph_2S_2, 882-33-7; $(C_6D_5)_2S_2$, 99397-58-7; $(p\text{-}MeC_6H_4)_2S_2$, 103-19-5; $(p\text{-}MeOC_6H_4)_2S_2$, 5335-87-5; $(p\text{-}ClC_6H_4)_2S_2$, 1142-19-4; azobis(diphenylmethane), 34863-14-4.

(36) In spite of repeated recrystallizations, the results of the elemental analyses of these products did not coincide staisfactorily with the calculated values (1–2% deviations in carbon). This is probably due to the thermally labile properties of these compounds. However, the ^{1}H NMR spectra could be assigned satisfactorily to the proposed structures.

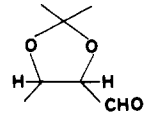
2,2,5-Trimethyl-1,3-dioxolane-4-carboxaldehyde as a Chiral Synthon: Synthesis of the Two Enantiomers of Methyl 2,3,6-Trideoxy-α-L-*threo*-hex-2-enopyranoside, Key Intermediate in the Synthesis of Daunosamine, and of (+)- and (−)-Rhodinose

Stefano Servi

CNR Centro di Studio per le Sostanze Organiche Naturali, Dipartimento di Chimica, Politecnico di Milano, 20133 Milano, Italy

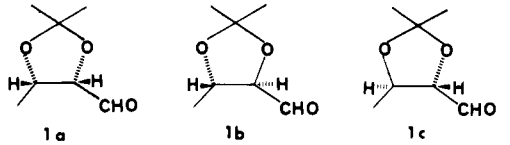
Received May 22, 1985

2,2,5-Trimethyl-1,3-dioxolane-4-carboxaldehyde (1) has proven to be a valuable chiral synthon in the preparation of optically active naturally occurring compounds.[1b] Thus,



1

chiron **1** has been used in synthetic methodologies as an alternative to tartaric, malic, and lactic acids and more often to carbohydrates. Moreover, aldehyde **1** is currently easily accessible in three of the possible stereoisomers,[2] i.e.,



[(4*S*)-cis] **1a** from the products obtained from cinnamaldehyde in fermenting bakers' yeast,[3] (4*R*-trans) **1b** from

(1) (a) This work has been financially supported by Piano Finalizzato CNR Chimica Fine e Secondaria. (b) See, for instance: Fuganti, C.; Servi, S.; Zirotti, C. *Tetrahedron Lett.* **1983**, 5285. Fuganti, C.; Grasselli, P.; Servi, S. *J. Chem. Soc., Chem. Commun.* **1982**, 1285. Servi, S. *Tetrahedron Lett.* **1983**, 2023.

(2) Although analytical data are elusive, the three aldehydes are relatively stable compounds and can be prepared in a reproducible way. Their absolute configuration and optical purity, has been proved by conversion into compounds of known absolute configuration (see ref 1–5).

0022-3263/85/1950-5865$01.50/0