N-Sulfonylaminyls. The Isolation of Dimers and Their Properties[1)]

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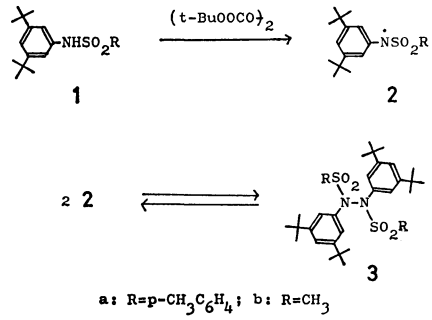
(Received January 9, 1981)

Synopsis. From the reaction mixtures of sulfonamides [3,5-$(t\text{-Bu})_2C_6H_3NHSO_2C_6H_4CH_3$-*p* and 3,5-$(t\text{-Bu})_2C_6H_3NHSO_2CH_3$] with di-*t*-butyl diperoxyoxalate, dimers of *N*-sulfonylaminyls were isolated as pure crystals which, in solution, dissociated into the corresponding *N*-sulfonylaminyls upon heating to 60 °C.

Since *N*-sulfonylaminyls ($R\dot{N}SO_3R'$) are important intermediates in organic and photochemical reactions,[2)] the radicals have been a subject of considerable interest and have been actively investigated by means of ESR spectroscopy.[3)] We have reported the ESR spectra of *N*-sulfonyl-(3,5-di-*t*-butylphenyl)aminyls (**2**), which are generated by the reaction of sulfonamides **1** with di-*t*-butyl diperoxyoxalate.[4)] Since *N*-sulfonylaminyls are transient species, it is quite difficult to isolate them in a pure form. However, the radicals may be isolated as dimers. If the dimers are isolated, we can confirm the assignments of their ESR spectra. Also, their chemical properties are of interest in connection with the structurally related dimers, **5** and **7**.[5,6)] For this purpose, we have carefully examined the products from the reaction of **1** with di-*t*-butyl diperoxyoxalate and have successfully isolated *N*-sulfonylaminyl dimers, **3**, in moderate yields. This is the first isolation of *N*-sulfonylaminyl dimers.[7)] In this report we will describe the isolation of **3** and their chemical properties.



In the general procedure, an oxygen-free benzene solution of **1** and di-*t*-butyl diperoxyoxalate (excess) was allowed to stand for 3 d at room temperature, after which the reaction mixture was concentrated and chromatographed on silica gel, using benzene as the eluent. The second band was collected and the solvent was evaporated to give crude **3** in 17—23% yields; this was then recrystallized from hexane: colorless crystals; yield, 12—17%. In the IR spectra of the crystals, no N–H absorptions were found, and the NMR spectra and the elemental analyses were satisfactrily consistent with the structures of **3**. Also, in the mass spectra, the peaks corresponding to ions of $M^+ + 1 - SO_2C_6H_4CH_3$ (for **3a**) and $M^+ - SO_2CH_3$ (for **3b**) were found, though molecular-ion peaks could not be detected. Thus, we identified the crystals as **3** dimers.

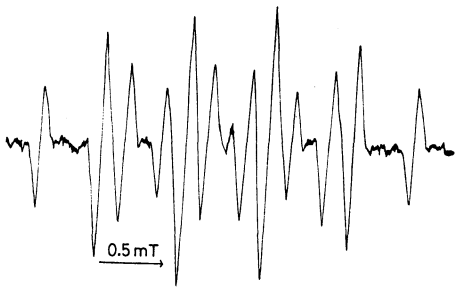
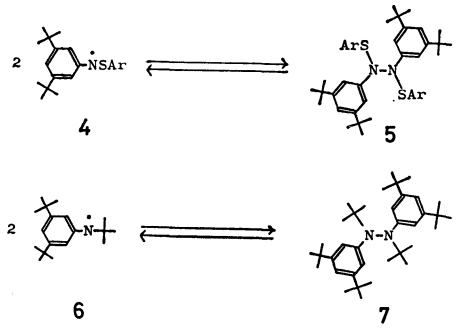


Fig. 1. ESR spectrum of **2b** detected from the solution of **3b** in benzene at 60 °C.

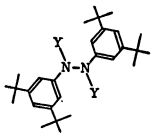
The dimers are highly soluble in most organic solvents, such as benzene, hexane, alcohols, and tetrahydrofuran, and the dimer solutions show no ESR signals. Thus, the dimers were found not to dissociate into **2** at room temperature. However, upon heating to 60 °C in benzene, the dimer solutions gave a relatively strong and clean ESR signal due to **2**, as is illustrated in Fig. 1; this finding clearly indicates that the dimer dissociate in part into **2** at this temperature. The assignments of the signals were based on their ESR parameters: a_N: 0.78; $a_{o\text{-}H}$: 0.56; $a_{p\text{-}H}$: 0.76 mT for **2a** and a_N: 0.77; $a_{o\text{-}H}$: 0.56; $a_{p\text{-}H}$: 0.77 mT for **2b**. These values are in good agreement with the previously reported values.[8)]

The equilibrium constants ([radical]^2[dimer]$^{-1}$) for the equilibria, however, are very small, even at 60 °C (probably$<10^{-9}$ mol l^{-1}). Also, upon heating at 60 °C in benzene for 2 h, trace amounts of the dimers were indicated by TLC analysis to decompose.



It is of interest to compare the equilibrium constants obtained for **3** with those reported for **5** and **7**. The reported values are 0.98×10^{-4}—4.59×10^{-4} mol l^{-1} for **5** (in benzene at 27 °C) and 6.00×10^{-6} mol l^{-1} for **7** (in methylcyclohexane at 44.7 °C). Thus, the magnitudes of the equilibrium constants of these dimers decrease in the following order: **5**>**7**>**3**. That is, when Y in **8** is an electron-donating group, –SR (dimers **5**). the equilibrium constants are remarkably increased, while when Y is an electron-withdrawing group,

$-SO_2R$ (dimers **3**), the equilibrium constants are, on the contrary, decreased. These changes in the magnitudes of the equilibrium constants may be reasonably interpreted as follows: in the case of **5**, the great electron-donating character of the –SR group enhances the dipolar repulsion between the nitrogen atoms, leading to a weakening of the nitrogen-nitrogen bond in **5**. In contrast, in the case of **3**, the electron-withdrawing character of the $-SO_2R$ group weakens the dipolar repulsion between the nitrogen atoms, leading to a strengthening of the nitrogen-nitrogen bond in **3**.



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Experimental

All the melting points were taken on a Yanaco Model MP melting-point apparatus and are uncorrected, The IR spectra were run on a JASCO Model IR-G spectrometer, while the ^1H NMR spectra were recorded with a JEOL PS-100 spectrometer, with tetramethylsilane as the internal standard. The mass spectra were obtained on either a JEOL JMS-D-300 (for **3a**) or a Hitachi M-60 mass spectrometer (for **3b**). The ESR spectra were recorded with a JEOL JES-ME-3X spectrometer equipped with an X-band microwave unit and 100 kHz field modulation. The temperature was controlled with a JEOL JES-VT-3A temperature controller. The field sweep was calibrated by using a JEOL Mn^{2+} reference sample. *N*-(3,5-Di-*t*-butylphenyl)-*p*-toluenesulfonamide (**1a**) and *N*-(3,5-di-*t*-butylphenyl)methanesulfonamide (**1b**) were prepared by the previously reported method,[4] and di-*t*-butyl diperoxyoxalate was obtained according to Bartlett's method.[9]

N,N′-Bis(3,5-di-t-butylphenyl)-N,N′-bis(p-tolylsulfonyl) hydrazine (3a).[10] Sulfonamide **1a** (500 mg, 1.39 mmol), di-*t*-butyl diperoxyoxalate (500 mg, 2.13 mmol), and benzene (10 ml) were placed in a glass tube (1.5×40 cm), and the mixture was degassed by three freeze-pump-thaw cycles and then sealed under a vacuum. After the sealed tube had been allowed to stand for 3 d at room temperature (≈20 °C), the benzene solution was washed twice with a 10% $Na_2S_2O_3$ aqueous solution and twice with water, and then dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure, and the residue was chromatographed on a silica-gel column (Mallinckrodt 100 mesh; column size: 3×50 cm), using benzene as the eluent. The second band was collected, and the solvent was evaporated to give 87 mg of crude **3a** (17%), which was afterward recrystallized from hexane to afford 61 mg of prisms (12%); mp 131—132 °C; (KBr): 2950—2850 (CH), 1160 cm^{-1} (SO_2); ^1H NMR (CCl_4) δ 1.20 (s, *t*-Bu, 36H), 2.42 (s, CH_3, 6H), 7.14—7.86 (m, aromatic, 14H); MS (70 eV), *m/e* (rel intensity), 562 ($M^+ + 1 - CH_3C_6H_4SO_2$, 6), 407 (10), 361 (20), 359 (100), 345 (24), 344 (98), 204 (42), 190 (20), 148 (20), 133 (44), 57 (37). Found: C, 70.71; H. 7.91; N, 3.74%. Calcd for $C_{42}H_{56}N_2O_4S_2$: C, 70.35; H, 7.87; N, 3.91%.

N,N′-Bis(3,5-di-t-butylphenyl)-N,N′-(methylsulfonyl) hydrazine (3b).[10] The hydrazine was prepared in a similar manner. Sulfonamide **1b** (400 mg, 1.41 mmol), di-*t*-butyl diperoxyxalate (500 mg, 2.13 mmol), and benzene (10 ml) were placed in a glass tube, degassed, and sealed as has been described above. After 3 d of standing at room temperature, the benzene solution was washed with a 10% $Na_2S_2O_3$ aqueous solution and then with water, and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated, and the residue was chromatographed on silica gel as has been described above. The second band was collected, and the solvent was evaporated to give 90 mg of crude **3b** (23%), which was then recrystallized from hexane to afford 68 mg of needles (17%); mp 130.5—131.5 °C; IR (KBr): 2950—2850 (CH), 1160 cm^{-1} (SO_2); ^1H NMR (CCl_4) δ 1.32 (s, *t*-Bu, 36H), 3.14 (s, CH_3, 6H), 7.15—7.39 (m, aromatic, 6H); MS (30 eV), *m/e* (rel intensity), 486 ($M^+ + 1 - CH_3SO_2$, 22), 485 ($M^+ - CH_3SO_2$, 47), 408 (28), 407 (54), 341 (22), 284 (25), 269 (52), 190 (70), 133 (29), 57 (100). Found: C, 63.50; H, 8.46; N, 5.06%. Calcd for $C_{30}H_{48}N_2O_4S_2$: C, 63.79; H, 8.57; N, 4.96%.

Dissociation of 3. The dimer, **3** (20 mg), and benzene (0.2 ml) were placed in an ESR cell, and the solution was degassed as has been described above. The ESR spectra from the solution were recorded during heating at 60 °C.

References

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2) For a review, see: R. S. Neale, *Synthesis*, **1971**, 1.

3) a) R. Istratoiu, I. Pascaru, and A. T. Balaban, *Z. Naturforsch., Teil B*, **28**, 543 (1973); b) G. Zomer and J. B. F. N. Engberts, *Tetrahedron Lett.*, **1977**, 3901; c) H. Teeninga and J. B. F. N. Engberts, *Recl. Trav. Chim. Pays-Bas*, **97**, 59 (1978); d) A. R. Forrester, E. M. Johansson, and R. H. Thomson, *J. Chem. Soc., Perkin Trans. I*, **1979**, 1112; e) H. Teeninga, B. Zomer, and J. B. F. N. Engberts, *J. Org. Chem.*, **44**, 4717 (1979); f) W. C. Danen and R. W. Gellert, *J. Am. Chem. Soc.*, **102**, 3264 (1980).

4) Y. Miura, Y. Nakamura, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **51**, 947 (1978).

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

6) S. F. Nelsen and R. T. Landis, *J. Am. Chem. Soc.*, **95**, 8707 (1973).

7) In Ref. 3d, the products derived from *N*-methoxy-*N*-sulfonylaminyl were carefully examined, but the radical dimer was not isolated.

8) For **2a**, a_N : 0.779; $a_{o\text{-}H}$: 0.564; $a_{p\text{-}H}$: 0.762 mT and for **2b**, a_N: 0.779; $a_{o\text{-}H}$: 0.559; $a_{p\text{-}H}$ 0.757 mT. See Ref. 4.

9) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

10) As has been pointed out in Ref. 9, it is advisable not to scrape the crystals of di-*t*-butyl diperoxyoxalate when treating them, especially when they are completely free of a solvent. Also, a large-scale experiment must be avoided in the preparation of the dimers, **3**.