Isolation and Characterization of Sulfonamidyl Radical Dimers[1]

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Received December 30, 1987

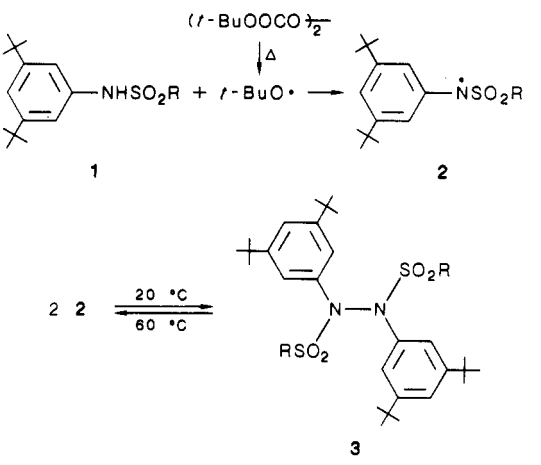
The dimers (**3a** and **3b**) of *N*-(3,5-di-*tert*-butylphenyl)benzenesulfonamidyl (**2a**) and -methanesulfonamidyl radicals (**2b**) have been isolated from the reaction of the corresponding sulfonamides with di-*tert*-butyl diperoxyoxalate and their physical and chemical behaviors have been investigated. The dimers in solution dissociate into the corresponding **2** above 60 °C. The $\Delta H°$ and $\Delta S°$ values for the **3a** $\rightleftarrows$ 2 **2a** equilibrium were determined to be 29.0 kcal/mol and 33.7 cal/deg·mol (in benzene), respectively, by means of ESR spectroscopy. Prolonged heating of **3** in solution leads to isomerization to N–C-coupled dimers. The reactions of **3** with azobis(diphenylmethane) and with 1,1-diphenylethylene were also examined. The thermodynamic parameters $\Delta H°$ and $\Delta S°$ are compared with those for structurally related aminyl radicals.

Sulfonamidyl radicals ($R\dot{N}SO_2R'$) are a considerably interesting intermediate in chemical and photochemical reactions,[2] and their electronic structures have been the recent interesting subject in the field of free radical chemistry. A variety of electron spin resonance (ESR) studies on sulfonamidyls,[3-10] as well as ab initio molecular orbital calculations,[11] have strongly indicated that the radicals are in a π-electronic ground state.

Since sulfonamidyl radicals are a transient species, it is almost impossible to isolate them as the radical crystals. Therefore, attempts were made to isolate the radicals as the corresponding dimers.[12,13] Balaban et al. reported that, on treating $PhSO_2NHOEt$ with $KMnO_4$, 1,2-bis(phenylsulfonyl)-1,2-diethoxyhydrazine could be isolated as the crystals.[12] Forrester et al. attempted to isolate the corresponding dimer by oxidation of *N*-methoxybiphenyl-2-sulfonamide with $Pb(OAc)_4$.[13] However, they could not detect the expected dimer from the reaction mixture by NMR spectroscopy. This discrepancy between the two reports might come from the thermal instability of the dimers of alkoxysulfonamidyl radicals. Indeed, the dimer isolated by Balaban et al. exhibited a sudden spontaneous decomposition upon standing at 25 °C for a few hours. Accordingly, owing to this thermal instability the dimer could not be fully investigated.

In the course of our ESR studies of a variety of nitrogen-centered free radicals, we have found that the dimers, **3a** and **3b**, of *N*-(3,5-di-*tert*-butylphenyl)benzenesulfonamidyl (**2a**) and -methanesulfonamidyl radicals (**2b**) can be isolated in moderate yields from the reaction mixture of the corresponding sulfonamides (**1a** and **1b**) and di-*tert*-butyl diperoxyoxalate.[14] Since these dimers are thermally stable, we could fully characterize them. Herein we report the results.

Scheme I[a]



[a] **a**: R = Ph; **b**: R = Me.

Results and Discussion

A mixture of sulfonamide **1** and di-*tert*-butyl diperoxyoxalate gives a relatively strong ESR spectrum at room temperature with the following ESR parameters:[15,16] a_N = 7.61, $a_{o\text{-}H}$ = 5.63, $a_{p\text{-}H}$ = 8.20 G (**2a**); a_N = 7.40, $a_{o\text{-}H}$ = 5.59, $a_{p\text{-}H}$ = 8.06 G (**2b**). When the mixture was allowed to stand for 2 days at room temperature under a nitrogen atmosphere, it gave, after column chromatographic separation, dimers **3** in 25–36% yields (Scheme I). The structures of the dimers were determined by the IR and ^1H NMR spectra and the elemental analyses. In the IR spectra no N–H absorption was found in the range 3300–3200 cm^{-1}, and the ^1H NMR spectra were completely assigned as the N–N-coupled (hydrazine-like) structure.

Dimers **3** are stable at ambient temperature without any detectable decomposition. However, when being heated to >60 °C, the dimer solution (benzene) gave a relatively strong ESR spectrum, as shown in Figure 1. The ESR parameters[15] for the spectra from the dimer solutions were within 0.08 G of those already given for the sulfonamidyls generated by reaction of **1** with di-*tert*-butyl diperoxy-

(1) ESR studies of nitrogen-centered free radicals. 32. Part 31: Miura, Y. *J. Org. Chem.*, in press.
(2) Neale, R. S. *Synthesis* **1971**, 1–15.
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(4) Zomer, G.; Engberts, J. B. F. N. *Tetrahedron Lett.* **1977**, 3901–3904.
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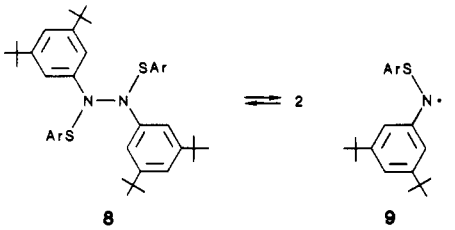
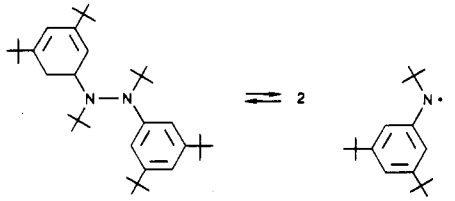
(6) Teeninga, H.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 59–60.
(7) Teeninga, H.; Zomer, B.; Engberts, J. B. F. N. *J. Org. Chem.* **1979**, *44*, 4717–4720.
(8) Danen, W. C.; Gellert, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 3264–3265.
(9) Sutcliffe, R.; Anpo, M.; Stolow, A.; Ingold, K. U. *J. Am. Chem. Soc.* **1982**, *104*, 6064–6070.
(10) Teeninga, H.; Engberts, J. B. F. N. *J. Org. Chem.* **1983**, *48*, 537–542.
(11) Teeninga, H.; Nieuwpoort, W. C.; Engberts, J. B. F. N. *Z. Naturforsch. B* **1981**, *36*, 279–281.
(12) Balaban, A. T.; Vasilescu, A. *Tetrahedron Lett.* **1972**, 571–574.
(13) Forrester, A. R.; Johansson, E. M.; Thomson, R. H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1112–1119.
(14) Miura, Y.; Nakamura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3217–3218.
(15) The hyperfine splitting constants are determined by computer simulation.
(16) The previously reported a_N and $a_{p\text{-}H}$ values for **2**,[5] which were determined without the aid of computer simulation, are 0.14–0.39 G higher and 0.53–0.64 G lower, respectively, than those in this work. These deviations in the magnitudes of a_N and $a_{p\text{-}H}$ are attributable to the missassignment of the ESR spectra in the previous work.[5]

0022-3263/88/1953-3012$01.50/0

Table I. Comparison of $\Delta H°$ and $\Delta S°$ Values for Some Dimer ⇄ Radical Equilibria

dimer	radical	$\Delta H°$, kcal/mol	$\Delta S°$, cal/deg·mol	ref
 **8**	**9**	13.3–13.8[a]	29.0–29.2[a]	19
 **10**	**11**	31.2	73.6	20
3a	2 **2a**	29.0	33.7	this work

[a] Ar: 4-tolyl or 4-chlorophenyl.

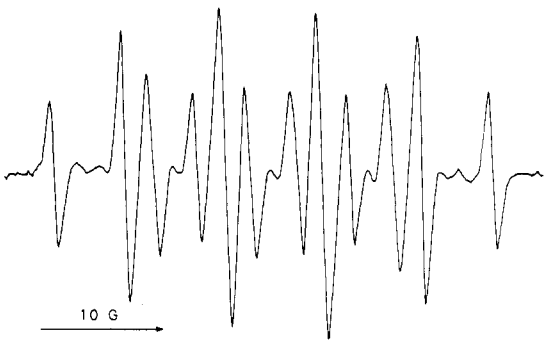


Figure 1. Experimental ESR spectrum of **2b** detected from a benzene solution of **3b** heated to 70 °C.

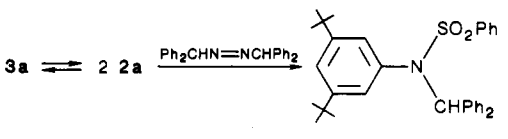
oxalate; these results strongly indicate that dimers **3** dissociate into the corresponding **2** radicals above 60 °C.

The equilibrium constants (K) for the **3a** ⇄ 2 **2a** equilibrium were measured in benzene in the temperature range 61–83 °C, and the enthalpy of dissociation ($\Delta H°$)

$$K = \frac{[\text{radical}]^2}{[\text{dimer}]}$$

and the entropy of dissociation ($\Delta S°$) for the equilibrium were calculated from the slope of a plot of ln K vs $1/T$ using the equation $-RT \ln K = \Delta H° - T\Delta S°$, where R is the gas constant and T is the absolute temperature. The values obtained are 29.0 ± 1.9 kcal/mol ($\Delta H°$) and 33.7 ± 6.0 cal/deg·mol ($\Delta S°$), respectively.

Since dimers **3** were found to dissociate into **2** at high temperature, some radical coupling reactions between **2** and azo compounds and between **2** and 1,1-diphenylethylene were examined. When **3a** was heated in benzene to 75 °C for 3 h in the presence of azobis(diphenylmethane), the reaction mixture afforded **4** in 23% yield.



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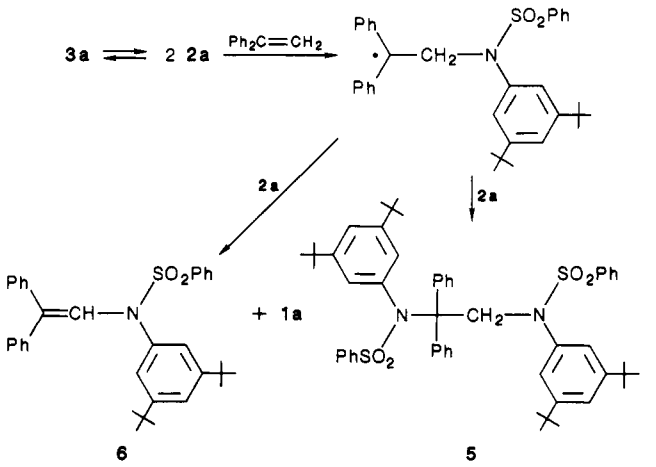
However, when 2,2′-azobis(isobutyronitrile) (AIBN) was employed instead of azobis(diphenylmethane), the reaction mixture gave no product expected from the radical coupling reaction between **2a** and 2-cyano-2-isopropyl radical, even after 17 h at 75 °C. The main product from the reaction was **1a** and the yield was 77%. From this result we infer that disproportionation between **2a** and 2-cyano-2-isopropyl, giving **1a** and 2-cyanopropene, predominantly occured.

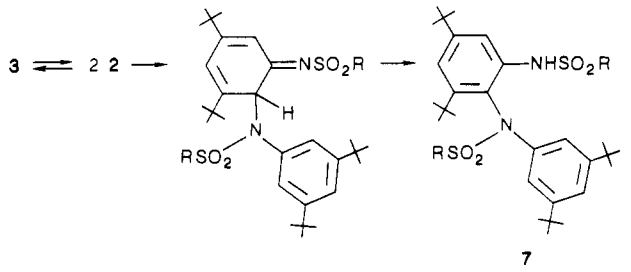
Scheme II



A mixture of **3a** and 1,1-diphenylethylene afforded, after 12 h at 75 °C, two adducts along with **1a** (14%). One of the adducts was a 1:2 adduct (**5**, 71%) of the alkene and **2a**, and the other was a 1:1 adduct (**6**, 14%) of the alkene and **2a**. The pathways leading to these products are outlined in Scheme II.

Although dimers **3** are stable at ambient temperature, prolonged heating converted **3** to the N–C-coupled compounds **7**. When a benzene solution of **3a** was heated to 60 °C for 3 h, 88–90% of the dimer was recovered, but 4–5% of the dimer isomerized to **7a**, and heating of a dimer solution to 80 °C for 3 h resulted in the 56–61% recovery of the dimer and the 30–35% conversion of the dimer to **7a**. On the other hand, when a benzene solution of **3b** was heated to 80 °C for 3 h, 88% of the dimer was recovered, but 10–13% of the dimer converted to **7b**. The structures of **7** were determined by the IR and ^{1}H NMR spectra and the elemental analyses. In the IR spectra of **7** a strong absorption due to ν_{N-H} was found at 3350 cm^{-1}, and in the

Scheme III[a]



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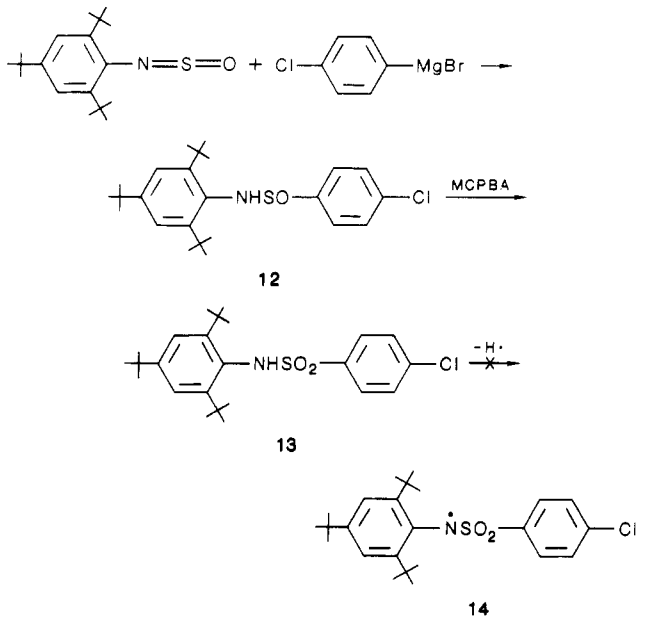
[a] a: R = Ph; b: R = Me.

^{1}H NMR spectra a singlet due to NH was found at δ 6.44 (**7a**) or 7.18 (**7b**). Furthermore, the four *tert*-butyl groups appeared as three singlets with the intensity ratio of 1:2:1,[17] and the two methyl groups in **7b** became magnetically nonequivalent.[17] On the basis of these spectral results the products were unequivocally identified as **7**. The mechanism for formation of **7** includes attack of **2** at the ortho position of the anilino benzene ring of another **2** molecule, followed by 1,3-hydrogen shift, as shown in Scheme III. The spin density on the ortho carbon of the anilino benzene ring, derived from $a_{o\text{-}H}$ (5.6 G) by using $\rho_c = Q/a_H$, where Q = −27 G,[18] is 0.21. Taking into account this high spin density on the position, the formation of **7** can be quite reasonably accounted for by the above mechanism.

In Table I, the $\Delta H°$ and $\Delta S°$ values for the **3a** ⇄ 2 **2a** equilibrium are compared with those for related dimer ⇄ radical equilibria. It is worthy to note that the $\Delta H°$ value for the **3a** ⇄ 2 **2a** equilibrium is close to that for the **10** ⇄ 2 **11** equilibrium.[20] However, it is ≈14 kcal/mol higher than that for the **8** ⇄ 2 **9** equilibrium.[19] As reported in a previous paper,[19] thioaminyl **9** is substantially stabilized by the conjugative delocalization of the unpaired electron from the nitrogen to the sulfur (-N̈-S̈- ↔ -N̈⁻-Ṡ⁺-). In contrast, a sulfonyl group, as well as a *tert*-butyl group, has no ability to delocalize the unpaired electron.[21] Accordingly, the hyperfine splitting constants for **2** are close to those for **11**[20,22] (a_N = 9.44, $a_{o\text{-}H}$ = 5.65, $a_{p\text{-}H}$ = 7.13 G). In general, the magnitudes of $\Delta H°$ for dimer ⇄ radical equilibria are dependent upon both structures of dimers and radicals. That is, in the case of hydrazine ⇄ aminyl radical equilibria, stabilization of the aminyls will reduce the $\Delta H°$ values, while a reduction of the dipolar repulsion between the two nitrogens of the hydrazines dimers will increase the $\Delta H°$ values. The results in Table I, however, strongly suggest that the magnitudes of $\Delta H°$ depend exclusively upon the structure of the aminyls, and the structures of the hydrazines are not important in determining the magnitudes of $\Delta H°$. This result is rather surprising, indicating that the strongly electron-accepting sulfonyl groups do not so significantly affect the nature of the N–N bond as to change the $\Delta H°$ value.

Finally, we prepared *N*-(2,4,6-tri-*tert*-butylphenyl)-4-chlorobenzenesulfonamide (**13**) by oxidation of sulfinamide **12** with *m*-chloroperbenzoic acid (MCPBA), since we expected that sulfonamidyl **14**, which might be derived from



13 by hydrogen-atom abstruction, might be persistent. As shown by its structure, the radical center is well protected by *tert*-butyl groups. Unfortunately, however, we could not generate this amidyl from **13** by any of the following procedures: oxidation with PbO_2, photolysis in the presence of di-*tert*-butyl peroxide, and reaction with di-*tert*-butyl diperoxyoxalate. We assume that this is attributable to destabilization of **14** caused by twisting of the anilino benzene ring.

Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Infrared (IR) spectra were run on a JASCO A-202 spectrophotometer. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a JEOL PS-100 (100 MHz) spectrometer. Chemical shifts (δ) are expressed in parts per million downfield from tetramethylsilane used as internal standard. Column chromatography was conducted on either silica gel (Wako gel C-200, 100–200 mesh) or alumina (Merck aluminum oxide 90, 70–230 mesh). TLC analyses were performed on Merck silica gel 60 F_{254} and/or Merck aluminum oxide 60 F_{254} plates and visualized with a short-wave UV lamp.

N-(3,5-Di-*tert*-butylphenyl)benzenesulfonamide (**1a**) and *N*-(3,5-di-*tert*-butylphenyl)methanesulfonamide (**1b**) were prepared by reaction of 3,5-di-*tert*-butylaniline with benzenesulfonyl or methanesulfonyl chloride in ether in the presence of triethylamine as previously reported.[5] Crystallization from hexane or benzene–hexane gave colorless prisms (**1a**) with mp 145–146 °C or colorless needles (**1b**) with mp 134–135 °C. 2,4,6-Tri-*tert*-butylsulfinaniline was obtained by reaction of 2,4,6-tri-*tert*-butylaniline with $SOCl_2$[23] and crystallized from 10:1 EtOH–H_2O; mp 114–116 °C (lit.[23] mp 120.5–122 °C). Azobis(diphenylmethane)[24] and di-*tert*-butyl diperoxyoxalate[25] were prepared according to the reported methods.

***N*,*N*′-Bis(3,5-di-*tert*-butylphenyl)-*N*,*N*′-bis(phenylsulfonyl)hydrazine (3a).** A mixture of 4.00 g (11.6 mmol) of **1a** and 4.0 g (17 mmol) of di-*tert*-butyl diperoxyoxalate (Caution! *do not scrape the crystals*) in 150 mL of benzene was stirred at

(17) In the ^{1}H NMR spectrum of **3a** the four *tert*-butyl groups are magnetically equivalent, and in that of **3b** the four *tert*-butyl groups and the two methyl groups are magnetically equivalent, respectively.

(18) Bruce, D. C.; Gilbert, C.; Hanson, P. *J. Chem. Soc., Perkin Trans. 2* **1977**, 517–525.

(19) Miura, Y.; Yamamoto, A.; Katsura, Y.; Kinoshita, M. *J. Org. Chem.* **1980**, *45*, 3875–3880.

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(21) Block, E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978; p 189.

(22) Although the a_N values for **2** are 1.80–2.0 G lower than that for **11**, it seems that the spin densities on the nitrogens of both radicals are approximately the same. The difference in the magnitudes of a_N seems to result from the difference in effectiveness of spin polarization for both radicals.

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(24) Cohen, S. G.; Wang, C. H. *J. Am. Chem. Soc.* **1955**, *77*, 2457–2460.

(25) Bartlett, P. D.; Benzing, E. P.; Pincock, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 1762–1768.

room temperature for 2 days under a slow stream of N_2. The resulting reaction mixture was washed with 10% $Na_2S_2O_3$ (50 mL × 2) and brine (50 mL) and dried over $MgSO_4$. After concentration to ca. 10 mL under reduced pressure, the residue was chromatographed on silica gel (column size 4.5 × 30 cm) with benzene as eluant. Crystallization from hexane gave 1.0–1.2 g (25–30%) of **3a** as colorless plates: mp 147–148 °C; TLC R_f 0.61 (silica gel, benzene) and 0.21 (alumina, 1:1 benzene–hexane); IR (KBr) 2950–2850 (*t*-Bu), 1165 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 1.16 (s, *t*-Bu, 36 H), 6.99–7.81 (m, Ar, 16 H). Anal. Calcd for $C_{40}H_{52}N_2S_2O_4$: C, 69.73; H, 7.61; N, 4.07. Found: C, 69.99; H, 7.64; N, 4.30.

N,N'-Bis(3,5-di-*tert*-butylphenyl)-N,N'-bis(methylsulfonyl)hydrazine (3b). A mixture of 3.80 g (13.5 mmol) of **1b** and 3.8 g (16 mmol) of di-*tert*-butyl diperoxyoxalate in 150 mL of benzene was stirred at room temperature for 2 days under a slow stream of N_2. The resulting reaction mixture was washed with 10% $Na_2S_2O_3$ (50 mL × 2) and brine (50 mL) and dried over $MgSO_4$. After concentration to ca. 10 mL under reduced pressure, the residue was chromatographed on silica gel (column size 4.5 × 20 cm) with benzene as eluant. Crystallization from hexane gave 1.35 g (36%) of **3b** as colorless needles: mp 130.5–131.5 °C; TLC R_f 0.42 (silica gel, benzene); IR (KBr) 2950–2850 (*t*-Bu), 1160 cm^{-1} (SO_2); ^1H NMR (CCl_4) δ 1.32 (s, *t*-Bu, 36 H), 3.14 (s, Me, 6 H), 7.15–7.39 (m, Ar, 6 H). Anal. Calcd for $C_{30}H_{48}N_2O_4S_2$: C, 63.79; H, 8.57; N, 4.96. Found: C, 63.50; H, 8.46; N, 5.06.

Reaction of 3a with Azobis(diphenylmethane). A solution of 200 mg (0.290 mmol) of **3a** and 1.05 g (2.9 mmol) of azobis(diphenylmethane) in 6 mL of benzene was heated at 75 °C for 8 h in a degassed glass tube in the dark. The reaction mixture was evaporated under reduced pressure and the residue was chromatographed on alumina (column size 3.5 × 37 cm) with 1:3 hexane–benzene as eluant. The pure fractions of *N*-(3,5-di-*tert*-butylphenyl)-*N*-(diphenylmethyl)benzenesulfonamide (**4**) were collected and evaporated under reduced pressure to give 75 mg (23%) of **4**. Crystallization from hexane afforded colorless needles with mp 137–139 °C; TLC R_f 0.65 (silica gel, benzene) and 0.40 (alumina, 1:1 benzene–hexane); IR (KBr) 2950–2850 (*t*-Bu), 1170 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 1.02 (s, *t*-Bu, 18 H), 6.74 (s, CH, 1 H), 6.35–7.73 (m, Ar, 18 H). Anal. Calcd for $C_{33}H_{37}NO_2S$: C, 77.45; H, 7.29; N, 2.74. Found: C, 77.74; H, 7.40; N, 2.90.

Reaction of 3a with 1,1-Diphenylethylene. A solution of 200 mg (0.290 mmol) of **3a** and 1.0 g (5.5 mmol) of 1,1-diphenylethylene in 6 mL of benzene was heated at 75 °C for 12 h in a degassed glass tube in the dark. The reaction mixture was evaporated under reduced pressure and ca. 10 mL of hexane was added to the residue. The colorless microcrystals of **5** deposited were collected by filtration and dried in vacuo (180 mg, 71%). TLC analysis of this product showed it to be pure.

The residual filtrate was evaporated under reduced pressure and the residue was chromatographed on silica gel (column size 3.5 × 30 cm). Elution with 1:5 benzene–hexane gave 1,1-diphenylethylene, and subsequent elution with benzene gave 42 mg (14%) of **6** and 29 mg of **1a**. Compound **1a** was identified by the melting point (142–144 °C) and the IR and ^1H NMR spectra.

N,N'-Bis(3,5-di-*tert*-butylphenyl)-N,N'-bis(phenylsulfonyl)-1,1-diphenylethylenediamine (5): colorless microcrystals; mp 198–200 °C (crystallized from benzene–hexane); TLC R_f 0.20 (silica gel, benzene); IR (KBr) 2950–2850 (*t*-Bu), 1170 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 1.01 (s, *t*-Bu, 18 H), 1.22 (s, *t*-Bu, 18 H), 3.99 (s, CH_2, 2 H), 6.09–7.75 (m, Ar, 26 H). Anal. Calcd for $C_{54}H_{64}N_2O_4S_2$: C, 74.61; H, 7.42; N, 3.22. Found: C, 74.87; H, 7.46; N, 3.26.

N-(3,5-Di-*tert*-butylphenyl)-N-(phenylsulfonyl)-2,2-diphenylethenamine (6): colorless needles; mp 140–141 °C (crystallized from hexane); TLC R_f 0.77 (silica gel, benzene); IR (KBr) 2950–2850 (*t*-Bu), 1160 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 1.10 (s, *t*-Bu, 18 H), 6.42–7.48 (m, olefinic and aromatic, 19 H). Anal. Calcd for $C_{34}H_{37}NO_2S$: C, 77.97; H, 7.12; N, 2.67. Found: C, 78.02; H, 7.27; N, 2.70.

Thermolysis of 3a. A solution of 200 mg (0.290 mmol) of **3a** in 10 mL of benzene was heated at 60 or 80 °C for 3 h in a degassed glass tube in the dark. The reaction mixture (yellow) was evaporated under reduced pressure and the residue was chromatographed on alumina (column size 3.5 × 18 cm). Elution with benzene gave **3a**, and subsequent elution with 1:50 EtOH–benzene gave product **7a**. The thermolysis was at least twice repeated at both 60 and 80 °C. The thermolysis at 60 °C gave 175–180 mg (88–90%) of **3a** and 8–10 mg (4–5%) of **7a**, while the thermolysis at 80 °C afforded 112–122 mg (56–61%) of **3a** and 59–70 mg (30–35%) of **7a**. The recovered **3a** was identified by the melting point (146–148 °C) and the IR and ^1H NMR spectra.

Product 7a: colorless needles; mp 201–203 °C (crystallized from hexane); TLC R_f 0.60 (silica gel, benzene) and 0.36 (alumina, 1:4 hexane–benzene); IR (KBr) 3350 (NH), 2950–2850 (*t*-Bu), 1160 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 1.20 (s, *t*-Bu, 9 H), 1.23 (s, *t*-Bu, 18 H), 1.44 (s, *t*-Bu, 9 H), 6.44 (s, NH, exchanged by D_2O, 1 H), 7.05–8.09 (m, Ar, 16 H). Anal. Calcd for $C_{40}H_{52}N_2O_4S_2$: C, 69.73; H, 7.61; N, 4.07. Found: C, 70.01; H, 7.51; N, 3.98.

Thermolysis of 3b. A solution of 200 mg (0.354 mmol) of **3b** in 10 mL of benzene was heated to 80 °C for 3 h in a degassed glass tube in the dark. The reaction mixture was evaporated under reduced pressure and the residue was chromatographed on silica gel (column size 3.5 × 10 cm). Elution with benzene gave **3b** (175 mg, 88%) and subsequent elution with 1:2 ethyl acetate–benzene gave product **7b** (20–25 mg, 10–13%). The thermolysis was repeated twice. The recovered **3b** was identified by the melting point (130.5–131.5 °C) and the IR and ^1H NMR spectra.

Product 7b: colorless plates; mp 216–217 °C (crystallized from hexane–benzene); TLC R_f 0.73 (silica gel, 1:100 EtOH–benzene); IR (KBr) 3350 (NH), 2950–2850 (*t*-Bu), 1160 and 1140 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 1.25 (s, *t*-Bu, 18 H), 1.35 (s, t-Bu, 9 H), 1.45 (s, *t*-Bu, 9 H), 2.31 (s, Me, 3 H), 3.37 (s, Me, 3 H), 7.18 (s, NH, exchanged by D_2O, 1 H), 7.08 (d, J = 1 Hz, Ar, 2 H), 7.17 (t, J = 1 Hz, Ar, 1 H), 7.48 (d, J = 2 Hz, Ar, 1 H), 7.71 (d, J = 2 Hz, Ar, 1 H). Anal. Calcd for $C_{30}H_{48}N_2O_4S_2$: C, 63.79; H, 8.57; N, 4.96. Found: C, 64.03; H, 8.78; N, 5.00.

N-(2,4,6-Tri-*tert*-butylphenyl)-4-chlorobenzenesulfinamide (12). A solution of (4-chlorophenyl)magnesium bromide, prepared by reaction of 9.6 g (50 mmol) of 4-chlorobromobenzene with 1.34 g (55 mg-atom) of Mg in 30 mL of dry THF, was added with a syringe to a solution of 1.54 g (5.1 mmol) of 2,4,6-tri-*tert*-butylsulfinaniline in 20 mL of dry THF at 0 °C with stirring. After being stirred at the same temperature for 1 h, the reaction mixture was poured into a saturated NH_4Cl solution (40 mL) and extracted with ether. The ether layer was washed with brine and dried over $MgSO_4$. After the solvents were removed on a rotary evaporator, the other volatile products were removed in vacuo to give a crystalline solid mass, which was crushed well in 10 mL of methanol and collected by filtration (1.53 g, 73%). Since this sulfinamide was thermally labile, purification was performed by reprecipitation; the sulfinamide was dissolved in a minimum amount (ca. 15 mL) of benzene and the benzene solution was poured into 200 mL of hexane and cooled to −20 °C overnight to give colorless prisms with mp 114–116 °C; IR (KBr) 3350 (NH), 2950–2850 (*t*-Bu), 1063 cm^{-1} (SO); ^1H NMR ($CDCl_3$) δ 1.31 (s, *t*-Bu, 9 H), 1.50 (s, *t*-Bu, 18 H), 6.35 (s, NH, 1 H), 7.36 (s, Ar, 2 H), 7.52 (d, J = 9 Hz, Ar, 2 H), 7.86 (d, J = 9 Hz, Ar, 2 H). Anal. Calcd for $C_{24}H_{34}ClNOS$: C, 68.62; H, 8.16; N, 3.34. Found: C, 68.85; H, 8.21; N, 3.44.

N-(2,4,6-Tri-*tert*-butylphenyl)-4-chlorobenzenesulfonamide (13). A mixture of 0.42 g (1.0 mmol) of **12** and 0.65 g (3.0 mmol) of *m*-chloroperbenzoic acid (80%) in 10 mL of CH_2Cl_2 was stirred at room temperature for 2 days. The reaction mixture was washed with 10% Na_2CO_3 solution (20 mL × 2) and brine (20 mL) and dried over $MgSO_4$. After concentration on a rotary evaporator, the residue was chromatographed on alumina (column size 3.5 × 10 cm) with 1:2 hexane–benzene as eluant. Crystallization from hexane gave 110 mg (25%) of **13** as colorless prisms with mp 179–180 °C; TLC R_f 0.50 (silica gel, benzene) 0.22 (alumina, 1:2 hexane–benzene); IR (KBr) 3300 (NH), 2950–2850 (*t*-Bu), 1165 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 1.25 (s, *t*-Bu, 18 H), 1.33 (s, *t*-Bu, 9 H), 6.37 (s, NH, 1 H), 7.06–7.31 (m, Ar, 6 H). Anal. Calcd for $C_{24}H_{34}ClNO_2S$: C, 66.10; H, 7.86; N, 3.21. Found: C, 66.36; H, 7.89; N, 3.38.

ESR Measurements. Dimer **3** (10–30 mg) and benzene (0.40 mL) were put into an ESR cell, and the solution was degassed by three freeze–pump–thaw cycles by using a high-vacuum system and the cell was sealed off. ESR spectra were recorded on a JEOL JES-FE-2XG spectrometer equipped with an X-band microwave unit and 100-kHz field modulation. Temperatures were controlled

with a JEOL ES-DVT1 controller. Estimated accuracy for the hyperfine splitting constants, ±0.1 G.

Measurements of Equilibrium Constants. A dimer solution (0.40 mL, 83.8 mM) was put into an ESR cell, and the solution was degassed by three freeze-pump-thaw cycles by using a high-vacuum system and the cell was sealed off. ESR spectra were recorded on a JEOL JES-FE-2XG spectrometer and double integration of the spectra was performed on a JEOL ES-9835B computer data system. Calibration curves were drawn with 1,3,5-triphenylverdazyl solutions[26] (6.92×10^{-7} to 2.05×10^{-6} M) using the same ESR cell and the same instrument settings as above. Equilibrium constants (K) were measured at three different temperatures between 61 and 83 °C, and the measurements were three times repeated. After measurement, all the samples were checked by TLC and it was confirmed that the amounts of the dimers decomposed during the time (ca. 15 min) necessary to measure radical concentrations at three different temperatures were a negligibly small quantity. The errors given refer to the maximum deviation from the average value.

Acknowledgment. We gratefully acknowledge Dr. H. Tanaka of Tokushima University for the measurement of the radical concentrations.

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Photostimulated Reaction of 1-Halo- and 1,4-Dihalobicyclo[2.2.2]octanes with Diphenylphosphide Ions by the $S_{RN}1$ Mechanism

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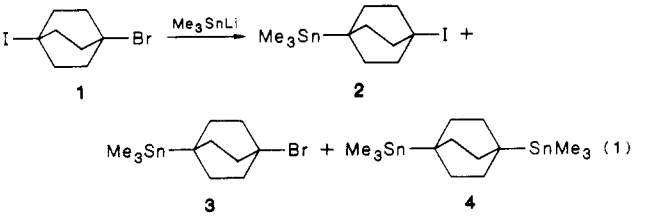
Received September 24, 1987

The reaction of 1-iodobicyclo[2.2.2]octane (**5**) with diphenylphosphide ions (**6**) in liquid ammonia gives in 20 min of irradiation and after oxidation of the reaction product good yields of (bicyclo[2.2.2]oct-1-yl)diphenylphosphine oxide (**8**). Although there is some reaction under dark conditions, the reaction is light catalyzed and inhibited by *p*-dinitrobenzene, a good inhibitor of $S_{RN}1$ reactions. However, 1-chlorobicyclo[2.2.2]octane (**9**) does not react under the same reaction conditions (240 min of irradiation). 1-Chloro-4-iodobicyclo[2.2.2]octane (**10**) gives only the monosubstitution product (4-chlorobicyclo[2.2.2]oct-1-yl)diphenylphosphine oxide (**12**), but 1-bromo-4-iodobicyclo[2.2.2]octane (**1**) and 1,4-diiodobicyclo[2.2.2]octane (**15**) give the disubstitution product **14**; the monosubstitution products are not intermediates of these reactions. It is suggested that these reactions occur by the $S_{RN}1$ mechanism of nucleophilic substitution at bridgehead positions.

Radical nucleophilic substitution ($S_{RN}1$ reaction) is a well-established process,[3] and several different types of substrates have been shown to react by this mechanism.[3,4] Among them there are reports in which halo bridgehead compounds substituted at the bridgehead position react with nucleophiles by the $S_{RN}1$ mechanism. For instance, 1-X-adamantanes (X = Cl, Br, I),[5,6] 9-bromotriptycene,[6] and 4-iodotricyclene[7] react with nucleophiles by this mechanism. However, 1-chlorobicyclo[2.2.1]heptane[8] and 4-chlorotricyclene[7] are unreactive under similar experimental conditions.

On the other hand, it has been reported that 1-bromo-4-iodobicyclo[2.2.2]octane (**1**) reacts with (trimethylstannyl)lithium in THF at 0 °C to give the three stannanes **2**-**4** in the ratio 3:1:3 (eq 1).[9]



It has been suggested that this reaction, along with others for additional 1,4-dihalobicyclo[2.2.2]octanes, occurs by a chain process similar to the $S_{RN}1$ mechanism but with an additional propagation step involving iodine atom abstraction from **1** by the 4-(trimethylstannyl)bicyclo[2.2.2]oct-1-yl radical intermediate to give **2** as product.[9b]

We now report the photostimulated reaction of 1-halo- and 1,4-dihalobicyclo[2.2.2]octanes with diphenylphosphide ions in order to determine the scope and limitations of these substrates in $S_{RN}1$ reactions.

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