DMSO; upon addition of base, the fluorescence shifts to orange ($\bar{v}_{max}$ 16,900 cm^{-1} $\pm$ 1%; FWHM = 3075 cm^{-1} $\pm$ 5%). Thus, X is not a likely emitter because of the low chemiluminescence efficiency observed and the spectral properties of IX.

Normal solvent shifts in fluorescence emission peaks are not accompanied by appreciable changes in FWHM.[8] If we postulate that the enzyme-bound excited-state product is only in a different effective dielectric from DMSO, we can correlate the yellow-green bioluminescence ($\bar{v}_{max}$ 17,700 cm^{-1}; FWHM = 2050 cm^{-1})[2] with emission from the dianion VIa in DMSO ($\bar{v}_{max}$ 18,000 cm^{-1}; FWHM = 2050 cm^{-1}).[9]

The very high base concentrations required to produce enolization of the excited keto anion (and thus yellow-green chemiluminescence in DMSO solutions) requires that in yellow-green bioluminescence the enolization must be enzyme catalyzed (as is initial anion formation at C-4). This might occur through C-5 proton extraction by one of the sulfhydryl groups (as an anion) at the active site.[10] Protonation of the mercaptide ion and also chelation by Zn^{2+}, Cd^{2+}, or Hg^{2+} would therefore explain the red bioluminescence observed in acidic solutions and in the presence of heavy metal ions.[11]

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Stereochemistry at Trivalent Nitrogen. V. Origin of Sulfur–Nitrogen Torsional Barriers in N-Sulfenylsulfonamides[1]

Sir:

Although the barriers to rotation about C–C single bonds are known to be low,[2,3] evidence has accumulated recently that substantial torsional barriers obtain about bonds between atoms which bear nonbonded valence

(1) Part IV: M. Raban and G. W. J. Kenney, Jr., submitted for publication.
(2) G. Binsch in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Interscience Publishers, New York, N. Y., Chapter 2.
(3) We restrict from consideration barriers which derive solely from steric hindrance (e.g., ortho-substituted biphenyls) or partial double bond character (e.g., amides).

electrons. Thus far, the systems studied using dynamic nmr spectroscopy[2] include sulfenamides,[4,5] aminophosphines,[6] disulfides,[7] trialkylhydroxylamines,[1] and the α-sulfinylcarbanion.[8,9]

One factor which has been implicated in these barriers is the coulombic repulsion between vicinal pairs of nonbonding valence electrons.[10] A theoretical study of the torsional barrier in an α-sulfinylcarbanion [HS(O)CH$_2$] has been performed.[8] The calculated transition states for torsion are ones in which the lone pairs of electrons on sulfur and carbon are *syn* and *anti* periplanar and the ground states are ones in which the dihedral angles between the nodal planes of the two filled nonbonding valence orbitals are close to 90°. This study also indicated a dependence on dihedral angle of the bond order of the S–C bond, although sulfur d orbitals were not involved. We report, here, experimental evidence which indicates that factors in addition to electron repulsion must be involved in determining the height of the torsional barrier in some sulfenamides.

We have investigated electronic effects on the barriers to conformational interchange in three series of N-arenesulfenyl-N-isopropylarenesulfonamides (1, 2, and 3).[11] In each case, the coalescence of resonances from diastereotopic isopropyl methyl protons is associated with a degenerate racemization reaction, which has as its rate-determining step torsion about the sulfenyl sulfur–nitrogen bond.[4,5,12] The coalescence temperature (T_c) was measured, the approximate rate at T_c calculated, and the free energy of activation (ΔG^*) at T_c obtained using the Eyring equation.[13] The relevant data are presented in Table I.

The magnitude of the effect of electronegativity was determined by obtaining linear least squares fit of experimental results to the free energy form of the Hammett equation:[14,15] $\Delta G^* = -2.3R\rho' + \Delta G^*_o$, where $\rho' = T\rho$. The data for series 1 fitted better when the point for 1* was omitted (Figure 1, Table II). The correlation coefficients obtained for 1 and 2 fall within the range judged to be acceptable correlations.

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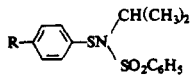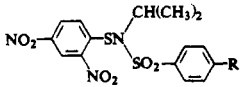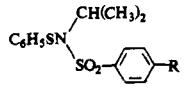(12) M. Raban, G. W. J. Kenney, Jr., J. M. Moldowan, and F. B. Jones, Jr., J. Am. Chem. Soc., 90, 2985 (1968).
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Table I. Nmr Parameters and Free Energies of Activation for Conformational Change

	Compound	R	$\sigma_p{}^a$	$\Delta\nu$, Hz	T_c, °C	ΔG^*, kcal/mol
	1a	OCH$_3$	−0.27	17.6	−15	13.2
R—⟨⟩—SN(CH(CH$_3$)$_2$)(SO$_2$C$_6$H$_5$)	1b	CH$_3$	−0.17	18	−20	12.9
	1c	H	0.00	17.8	−8	13.5
	1d	Cl	0.23	18.5	0	13.9
	1e	NO$_2$	0.78	18.1	32	15.6
NO$_2$—⟨⟩—SN(CH(CH$_3$)$_2$)(SO$_2$—⟨⟩—R) NO$_2$	2a	CH$_3$	−0.17	19.2	101	19.3
	2b	H	0.00	20.0	99	19.1
	2c	NO$_2$	0.78	18.8	31.5	15.6
C$_6$H$_5$SN(CH(CH$_3$)$_2$)(SO$_2$—⟨⟩—R)	3a	CH$_3$	−0.17	16.7	−11	13.4
	3b	H	0.00	17.8	−8	13.5
	3c	Cl	0.23	17.2	−16.5	13.6
	3d	NO$_2$	0.78	15.4	−10.5	13.4

^{a} Taken from ref 14c.

Table II. Correlation of Free Energy of Activation with Hammett Substituent Constants

| Series	$\rho'{}^b$	$\rho_{300}{}^b$	R^c
1	−554 ± 60	−1.9 ± 0.2	0.979
1^a	−617 ± 40	−2.1 ± 0.1	0.996
2	889 ± 121	3.0 ± 0.4	−0.991
3	11 ± 25	0.0 ± 0.1	−0.300

^{a} Excluding data for 1a. ^{b} Error ranges are linear least squares standard deviations. ^{c} Correlation coefficient.
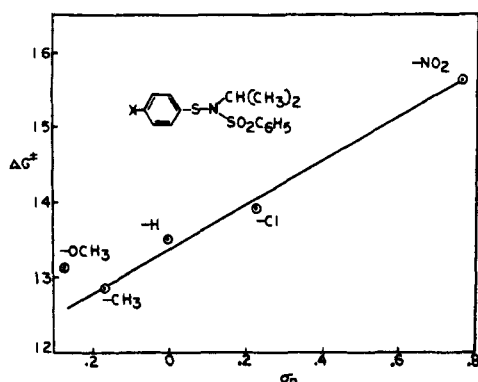
Figure 1. Hammett plot of free energies for degenerate racemization in series 1.

Were electron repulsion the sole contributor to the torsional barrier, an increase in the electronegativity of substituents attached to either sulfur or nitrogen would be expected to result in a decrease in the barrier (i.e., positive ρ') if any dependence is observed at all. Although a positive ρ' is observed in series **2**, the ρ' observed in **1** is negative and equals zero for series **3**. Clearly additional factors must be involved.

Although further work is necessary to verify our interpretation, we regard the low barriers in series **3** as arising substantially from electron repulsion. The attachment of electronegative groups to sulfur provides an additional contribution to the torsional barrier. The difference in the sign of ρ' for groups at nitrogen and sulfur implies that electron donation from nitrogen to sulfur is accompanied by an increase in the torsional barrier or that the opposition of the C–S and nitrogen-lone pair dipoles confers considerable stabilization. Although p–d π bonding would seem to be a possible

explanation, a dependence of p–d bonding on dihedral angle is not expected.[16−19] Further, the theoretical calculation of the torsional barrier in the α-sulfinylcarbanion indicated that sulfur d orbitals were not involved in the dependence of bond order on dihedral angle.[8] A possible alternative is that the orbital containing the nitrogen lone pair of electrons can overlap with the orbital that sulfur uses to form the S–C bond or with the corresponding σ^* orbital. This overlap would be possible only when the lone pair on nitrogen and the sulfur–carbon bond are coplanar and hence stabilizes the ground state (**1-G**) but cannot occur in the transition state (**1-T**), thus increasing the torsional barrier.

1-G   **1-T**
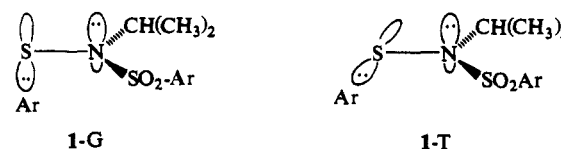
The electronegativity effects can be easily explained in terms of either hypothesis. The presence of an electronegative substituent on sulfur is necessary for the creation of a substantial C–S bond dipole or overlap between the lone pair and an orbital on sulfur, and an increase in electron withdrawal increases the magnitude of the stabilization in the ground state and hence the barrier to rotation. The deviation of the point for compound **1a** from the line (Figure 1) may occur because a minimum barrier of ca. 13 kcal/mol is provided by electron repulsion and steric considerations. Only when electronegative substituents are present in the sulfenyl phenyl ring does the torsional barrier respond to changes in the electronegativity of substituents in the sulfonyl phenyl ring.

Although our results are not yet definitive, they do indicate that barriers to rotation around formal single bonds between heteroatoms can be as large as ca. 20 kcal/mol and that the origin of these barriers must involve factors in addition to the electron repulsion and

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The Spin Resonance Spectrum and Reactivity of the *t*-Butoxy Radical

Sir:

There are several reports in the literature of attempts to observe the esr spectrum of the *t*-butoxy radical $(BO\cdot)$ generated by photolysis of di-*t*-butyl peroxide[1-3] (BOOB) or *t*-butyl hydroperoxide (BOOH).[2-5] Piette and Landgraf[4] irradiated BOOH and observed a one-line spectrum with $g = 2.003$. However, later work indicated that the radical observed was $BOO\cdot$, rather than $BO\cdot$,[2,3] and no esr signal was detected on irradiation of carefully purified BOOB.[2] We now find that on irradiation of freshly washed and distilled BOOB, using a high-intensity source and fairly efficient focusing of the light,[6] we observe a one-line spectrum with $g = 2.004 \pm 0.004$. On the other hand, irradiation of 10% BOOH in BOOB produces a radical having a one-line spectrum with $g = 2.015 \pm 0.004$. The latter value is in excellent agreement with the values of 2.014 ± 0.001 for $BOO\cdot$[3,7] and 2.0146 ± 0.0001 for $C_6H_5C(CH_3)_2OO\cdot$.[8] Irradiation of solid BOOB at $-70°$ produced a radical at $g = 2.004 \pm 0.004$ and a peak to peak width of 12 G.

followed to 60–70% destruction of the radical. The results were plotted according to eq 1. The number of

$$R_0/R = 1 + 2(k_t R_0)t \qquad (1)$$

points in each plot is listed in column 4. The absolute steady-state radical concentration, R_0, in run 1 was determined by double electronic integration using standard pitch as the reference.[6] In runs 2–6 the values of R_0 were determined by comparing the derivative peak heights with that of run 1. The average value thus obtained for k_t is $1.3 \times 10^9 \ M^{-1} \sec^{-1}$. Several estimates of k_t for $BO\cdot$ have been based upon indirect kinetic studies. Walling and Kurkov have estimated k_t as $1.4 \times 10^9 \ M^{-1} \sec^{-1}$ in carbon tetrachloride solution by measuring the per cent cage reaction in the decomposition of *t*-butyl hypochlorite and using eq 2 with iodine atom as the standard.[9]

$$k_{t,BO\cdot} = \frac{a_{BO\cdot}}{a_{I\cdot}} k_{t,I\cdot} \qquad (2)$$

$$a = \text{per cent cage reaction}$$

Ingold and Carlsson have arrived at a value of $2.8 \times 10^8 \ M^{-1} \sec^{-1}$ based on oxidation studies.[10] There is also a report that 10% of the radicals produced in the decomposition of BOOB in isooctane undergo geminate recombination. This would lead to a value of k_t of $10^9 \ M^{-1} \sec^{-1}$ ($k_t = Ak_D$, $k_D \approx 10^{10} \ M^{-1} \sec^{-1}$). By way of contrast, the observed termination constant for $BOO\cdot$ at 30° can be extrapolated from the data of Maguire and Pink to be $3.0 \times 10^5 \ M^{-1} \sec^{-1}$.[2] There are several values of k_t for $C_6H_5C(CH_3)_2OO\cdot$ in the literature.[8,11,12] The values obtained by esr spectroscopy are $2.2 \times 10^4 \ M^{-1} \sec^{-1}$ and $3.7 \times 10^4 \ M^{-1} \sec^{-1}$, while that obtained from oxidation studies is $0.75 \times 10^4 \ M^{-1} \sec^{-1}$.[12] The Russell mechanism for termination of peroxy radicals outlined below shows that the observed rate constant is equal to $k_3 k_4/(k_{-3} + k_4)$.[12-14] The vast difference in k_t values
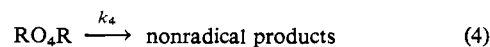
$$2RO_2\cdot \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} RO_4R \qquad (3)$$

Table I. Termination Constant for *t*-Butoxy Radical

Run	% destruction	Termination time[a] $\times 10^3$ sec	No. of points	r[b]	Intercept[c]	$kR_0 \times 10^{-3}$ sec^{-1}	$R_0 \times 10^6$ M	$k \times 10^{-9}$ M^{-1} sec^{-1}
1	66	2.2	4	0.991	0.94	2.02	1.5±.3	1.4
2	68	2.2	4	0.982	0.83	1.64	1.5	1.1
3	68	2.2	6	0.986	1.02	1.18	1.0	1.2
4	68	2.2	5	0.981	0.78	2.50	2.0	1.3
5	60	5.1	4	0.989	0.94	3.09	2.0	1.5
6	43	2.2	4	0.982	0.97	2.16	1.6	1.4

[a] Time allowed for decay. [b] Correlation coefficient for the least squares line. [c] The intercept should be 1.00.

Using techniques previously described[6] we followed the decay of the signal with $g = 2.004$ at room temperature. The results are reported in Table I. The decay was

$$RO_4R \xrightarrow{k_4} \text{nonradical products} \qquad (4)$$

for $BO\cdot$ and $BOO\cdot$ is due to the fact that $k_{-3} \gg k_4$.[7] When R is benzyl, k_t has been estimated as $1.5 \times 10^8 \ M^{-1} \sec^{-1}$.[15] This increase is associated with an in-

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