Torsional Diastereomerism in *N*-Arenesulfonyl-*N*-alkylsulfenamides[1]

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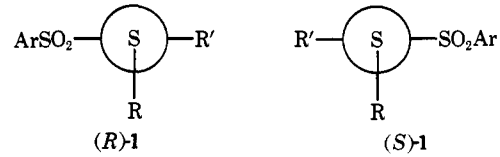
Abstract: *N*-Arenesulfonyl-*N*-(1-arylethyl)sulfenamides [$RSN(SO_2Ar)CH(CH_3)Ar'$] possess two units of chirality, an asymmetric carbon atom in the side chain and the stereolabile chiral axis of the sulfenamide S–N bond. Because rotation about the sulfenamide bond is slow on the nmr time scale at accessible temperatures, the nmr spectra of these compounds are those of equilibrium mixtures of diastereomers. At higher temperatures signals from the two diastereomers coalesce as epimerization at the sulfenamide chiral unit becomes rapid on the nmr time scale. Nmr line-shape analysis at the coalescence temperature furnished rates of epimerization and hence free energies of activation at the coalescence temperatures. Equilibrium constants and free energies of activation for the seven compounds examined were: R = CCl_3, Ar = Ar′ = C_6H_5 (1.1, 17.2 kcal/mol); R = C_6H_5, Ar = Ar′ = C_6H_5 (1.0, 13.0 kcal/mol); R = *p*-$CH_3C_6H_4$, Ar = Ar′ = C_6H_5 (1.0, 12.2 kcal/mol); R = CCl_3, Ar = *p*-$CH_3C_6H_4$, Ar′ = C_6H_5 (1.1, 17.4 kcal/mol); R = 2,4-$(NO_2)_2C_6H_3$, Ar = *p*-$CH_3C_6H_4$, Ar′ = C_6H_5 (2.4, 19.7 kcal/mol); R = *o*-$(NO_2)C_6H_4$, Ar = *p*-$CH_3C_6H_4$, Ar′ = C_6H_5 (1.9, 18.4 kcal/mol); R = CCl_3, Ar = C_6H_5, Ar′ = 1-naphthyl (1.9, 18.3 kcal/mol). The rate of epimerization for one compound (R = CCl_3, Ar = Ar′ = C_6H_5) was obtained by isolating a single diastereomer and using conventional kinetic methods in the region of −48 to −65° and by complete line-shape analysis in the temperature range 28–92°. Activation parameters were obtained: $\Delta H^{\pm}$ = 15.2 kcal/mol, $\Delta S^{\pm}$ = −7 eu, E_a = 15.8 kcal/mol, and log A = 11.7. The results were interpreted on the basis of steric and polar effects on both the equilibrium constants and the torsional barriers.

The discovery of substantial barriers to rotation about bonds between atoms with nonbonded valence electrons has provided a new dimension to the stereochemistry of compounds containing bonds between nitrogen and, *inter alia*, phosphorus,[3] oxygen,[4] nitrogen,[5] and sulfur.[6] Among these classes of compounds, the *N*-arenesulfonyl-*N*-alkylsulfenamides feature the highest torsional barriers.[7] The barrier to rotation about the S–N bond in sulfenamides renders the sulfenamide moiety an element of axial chirality, analogous to the axial chirality of 1,3-disubstituted allenes. The geometry of the sulfenyl moiety in *N*-arenesulfonyl-*N*-alkylsulfenamides, as evidenced by single-crystal X-ray diffraction,[8] is approximated by the Newman projections (R)-**1** and (S)-**1**,[9] since the ligands at nitrogen very nearly lie in a common plane with the nitrogen atom.



(*R*)-**1** (*S*)-**1**

When an *N*-arenesulfonylsulfenamide is prepared with an R′ substituent containing an asymmetric carbon atom, the presence of the additional chiral unit introduces the possibility of diastereomerism. However, the barrier to stereomutation at the sulfenyl chiral unit is only on the order of 12–20 kcal/mol. As a result, epimerization by rotation about the sulfur–nitrogen bond is rapid on the isolation time scale at room temperature. Although stereomutation is rapid on the isolation time scale, it is slow enough on the nmr time scale that spectra can be taken below the point of coalescence. Such spectra feature nonequivalent signals for corresponding groups in the two diastereomers.[10] The ratios of intensities of such signals afford measures of the equilibrium constants for torsional epimerization. Examination of these compounds by variable-temperature nmr spectroscopy can also furnish rates of torsion about the S–N bond in the temperature range in which coalescence of signals from corresponding groups in the two diastereomers occurs. In addition, conventional kinetics can be used to mea-

(1) (a) Stereochemistry in Trivalent Nitrogen Compounds. XVI. Part XV: M. Raban and T. Cho, *Int. J. Sulfur Chem.*, in press. (b) A portion of this work has been presented in preliminary form: M. Raban, G. W. J. Kenney, Jr., J. M. Moldowan, and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **90**, 2985 (1968). (c) Taken in part from the Ph.D. Thesis of F. B. Jones, Jr., Wayne State University, 1970, and the M.S. Thesis of S. K. Lauderback, Wayne State University, 1970. (d) We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) (a) University Fellow, 1971–1972; (b) National Science Foundation Undergraduate Research Participant, 1968; (c) University Fellow, 1969–1970.

(3) A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, **92**, 1085, 5206 (1970); H. Goldwhite and D. G. Rowsell, *Chem. Commun.*, 713 (1969).

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(6) (a) M. Raban, G. W. J. Kenney, Jr., and F. B. Jones, Jr., *Tetrahedron Lett.*, 5055 (1968); (b) J. M. Lehn and J. Wagner, *Chem. Commun.*, 1298 (1968); (c) M. Raban, F. B. Jones, Jr., and G. W. J. Kenney, Jr., *J. Amer. Chem. Soc.*, **91**, 6677 (1969).

(7) M. Raban and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **93**, 2692 (1971).

(8) J. Kay, M. Glick, and M. Raban, *ibid.*, **93**, 5224 (1971).

(9) The application of the Cahn–Ingold–Prelog rules to the specification of absolute configuration at the sulfenyl chiral axis requires the assignment of a phantom atom (p) to augment the substitution at sulfur to triligancy, in order that the analogy to allenes be satisfied. The phantom ligand lies in the R–S–N plane on the side opposite to the R group. When R′ is an alkyl or aryl group, the priority used in applying the sequence rule is R > p > $ArSO_2$ > R′, or equivalently $ArSO_2$ > R′ > R > p.

(10) M. Raban and K. Mislow, *Tetrahedron Lett.*, 3961 (1966).

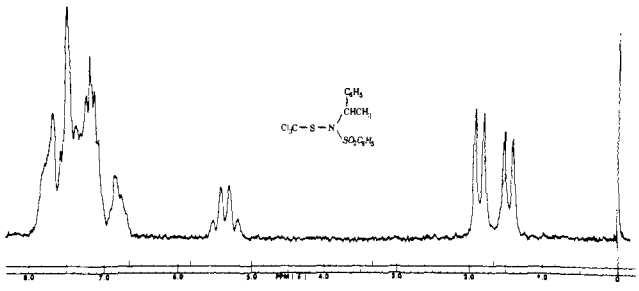
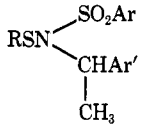


Figure 1. Room temperature nmr spectrum of **2a** in chloroform-*d*.

sure the much slower rates of conversion of a single diastereomer to an equilibrium mixture on the isolation time scale at temperatures about 100° below the coalescence temperature. The use of both methods makes possible the determination of reliable activation parameters.[11]

Results

A series of *N*-arenesulfonyl-*N*-alkylsulfenamides (**2**) was prepared by reaction of the lithium salts of three *N*-alkylsulfonamides with trichloromethanesulfenyl chloride and representative arenesulfenyl chlorides. All exhibited chemical-shift nonequivalence of diastereotopic groups at temperatures below their coalescence points. As an example *N*-1-phenylethyl-*N*-(benzenesulfonyl)trichloromethanesulfenamide (**2a**) exists in solution at room temperature as a mixture of diastereomers, (*R,R*)-**2a** and (*R,S*)-**2a** [and their enantiomeric set (*S,S*)-**2a** and (*S,R*)-**2a**].[12] The room temper-



2a, R = CCl_3; Ar = Ar′ = C_6H_5
b, R = C_6H_5; Ar = Ar′ = C_6H_5
c, R = *p*-$CH_3C_6H_4$; Ar = Ar′ = C_6H_5
d, R = CCl_3; Ar = *p*-$CH_3C_6H_4$; Ar′ = C_6H_5
e, R = 2,4-$(NO_2)_2C_6H_3$; Ar = *p*-$CH_3C_6H_4$; Ar′ = C_6H_5
f, R = *o*-$(NO_2)C_6H_4$; Ar = *p*-$CH_3C_6H_4$; Ar′ = C_6H_5
g, R = CCl_3; Ar = C_6H_5; Ar′ = 1-naphthyl

ature nmr spectrum in chloroform-*d* (Figure 1) reflects the presence of two diastereomers in equilibrium in the region of the *C*-methyl groups featuring two methyl doublets corresponding to (*R,R*)-**2a** and (*R,S*)-**2a** in a ratio of 1.2:1. At higher temperatures the *C*-methyl signals broaden, coalesce, and finally sharpen to a single doublet as the rate of rotation about the N–S single bond becomes rapid on the nmr time scale. The rates of rotation were measured at a series of 16 temperatures between 28 and 92° using complete line-shape analysis employing a computer program for simulation of spectra based on a subspectral analysis of the coalescing doublets system.[7] Experimental and theoretical spectra are illustrated in Figure 2.

The rates of torsion about the N–S bond were also measured by conventional kinetics in the temperature range −48 to −65°. The crystallization of **2a** is accompanied by second-order asymmetric transforma-

(11) M. Raban and E. H. Carlson, *J. Amer. Chem. Soc.*, **93**, 685 (1971).

(12) Since enantiomers give rise to identical nmr spectra in achiral solvents the presence of the enantiomeric pair does not give rise to additional signals and consequently we can ignore its presence in this and subsequent discussions.

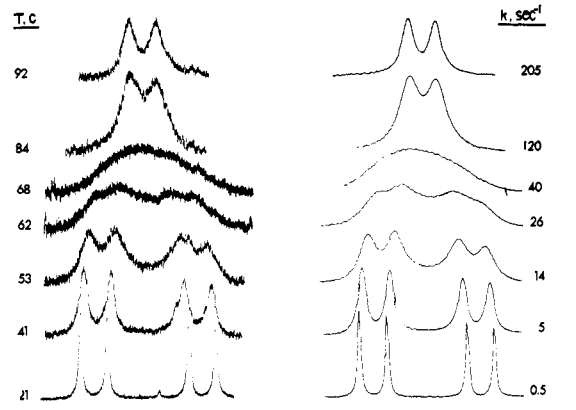


Figure 2. Experimental and theoretical nmr spectra of **2a** in methylene chloride

tion. One of the isomers of **2a** is more easily crystallized and as crystallization occurs the mobile equilibrium between the (*R,S*) and (*R,R*) isomers is displaced so that all of the crystalline material is composed of a single epimer. When the crystals are dissolved at room temperature, epimerization is rapid (on the isolation time scale) and equilibrium is attained virtually instantaneously. However, on the basis of the free energy of activation for torsion at the coalescence temperature (T_c = 68°, $\Delta G^{\ddagger}$ = 17.2 kcal/mol) we could calculate that epimerization could be slowed on the isolation time scale below about −70°. Accordingly, a sample of crystalline **2a** was dissolved in methylene chloride at temperatures below −70°, and the nmr spectrum was measured without prior warming. The initial spectrum featured only the presence of the downfield methyl doublet indicating that only a single diastereomer was present in solution. When the temperature was raised to −65°, epimerization on the isolation time scale began to occur at a measurable rate and could be monitored by the appearance and rate of growth of the upfield methyl doublet. Ratios of the two isomers were measured by integration of nmr signals over periods of up to 3 hr at four temperatures in the range −48 to −65°. The data were fitted to the rate equation for reversible first-order reaction using a linear least-squares program. The temperature dependence of the first-order rate constants so obtained was analyzed using Arrhenius (ln *k vs.* $1/T$) or Eyring (ln $[k/T]$ *vs.* $1/T$) linear least-squares correlation.

These low-temperature rate data were supplemented with the data from complete line-shape analysis in the range of signal broadening (28–92°). Eyring and Arrhenius correlations were made using the high-temperature data and using a combined set of data in both temperature ranges. The results of analysis of all three sets of data are collected in Table I and the Eyring plot of the combined data set is shown in Figure 3. Since the calibration of the "methanol and ethylene glycol thermometers" described in the Varian manual has been questioned,[13] we have reported activation parameters obtained using both calibration curves. All of the analyses furnish moderately small negative entropies of activation and we feel the most reliable value is that obtained using both data sets since random errors as

(13) (a) A. L. Van Geet, *Anal. Chem.*, 40, 2227 (1968); (b) A. L. Van Geet, *ibid.*, 42, 679 (1970).

Table I. Activation Parameters for Torsion about the N–S Bond in **2a**[a]

Temp range, °C	Method[b]	Temp[c] calibration	$\Delta G^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	E_a, kcal/mol	Log A, sec^{-1}
−65 to −48	CK	V	16.7–16.8	15.5 ± 0.5	−5 ± 2	16.0 ± 0.5	12.0 ± 0.5
−68 to −50	CK	G	16.5–16.7	14.1 ± 0.9	−10 ± 4	14.6 ± 0.9	10.7 ± 0.9
28 to 92	CLA	V	17.4–17.7	16.2 ± 0.4	−3 ± 1	17.0 ± 0.4	12.5 ± 0.2
28 to 95	CLA	G	17.4–17.8	15.8 ± 0.4	−5 ± 1	16.6 ± 0.4	12.1 ± 0.2
−65 to 92	CK and CLA	V	16.7–17.7	15.2 ± 0.1	−6.7 ± 0.4	15.8 ± 0.1	11.7 ± 0.1
−68 to 95	CK and CLA	G	16.5–17.8	14.7 ± 0.1	−8.5 ± 0.4	15.3 ± 0.1	11.3 ± 0.1

[a] Error ranges are linear least-squares standard deviations. [b] CLA, complete line-shape analysis; CK, conventional kinetics. [c] V, using methanol and ethylene glycol spectra as described in the Varian manual; G, using methanol and ethylene glycol spectra and the temperature calibration charts and equations of Van Geet.[13]

Table II. Nmr Spectral Data for Compounds **2**

Compd	Solvent	$\Delta\nu$,[a] Hz	T_c,[b] °C	K_{eq}	$\Delta G^{\ddagger}$, kcal/mol	k_c,[c] sec^{-1}	$\Delta H^{\ddagger}$[d], kcal/mol	k^d (27°), sec^{-1}
2a	CH_2Cl_2	27.0	68.0	1.1	17.2	73	14.9	3.2
2b	$CDCl_3$	16.5	−17.5	1.0	13.0	40	11.3	1260
2c	$CDCl_3$	9.4[e]	−38.0	1.0	12.2	23	10.6	4070
2d	Toluene-d_8	32.0	70.5	1.1	17.4	60	15.1	2.1
2e	Toluene-d_8	19.0	102.5	2.4	19.7	29	17.1	0.071
2f	Toluene-d_8	13.0	75.0	1.9	18.4	20	16.1	0.410
2g	CH_2Cl_2	20.5	78.0	1.9[f]	18.3	31	15.9	0.540

[a] Chemical-shift difference between methyl doublets unless otherwise indicated. [b] Temperatures determined by calibration with methanol or ethylene glycol spectra as outlined in the Varian manual. [c] Rate constants were determined by interpolation using calibration curves derived from complete line-shape analysis. In all cases, the free energy of activation refers to the conversion of the less stable into the more stable diastereomer. [d] Obtained from the experimental free energy of activation assuming $\Delta S^{\ddagger} = -6.7$ eu (see text). [e] Chemical-shift difference between *p*-tolylmethyl singlets. [f] The same equilibrium constant was observed in toluene-d_8.

well as systematic errors in the dnmr method are rendered less important by the large temperature range (over 150°). Although the Varian and Van Geet thermometers yield slightly different data, the differences are not large enough to affect our interpretation. The

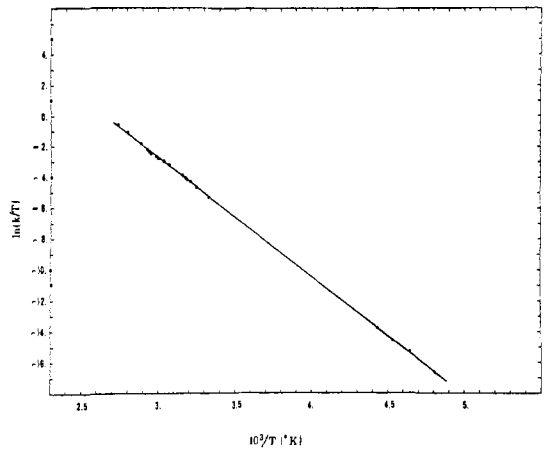


Figure 3. Eyring plot of rate–temperature data for **2a** in the temperature range −65 to 92°.

values obtained using both data sets and the Varian calibration ($\Delta H^{\ddagger} = 15.2 \pm 0.1$ kcal/mol, $\Delta S^{\ddagger} = -6.7 \pm 0.4$ eu) indicate a moderate negative entropy of activation. In contrast to large entropies of activation often obtained using dnmr, which in some cases arise from systematic errors in the analysis, we believe that ours is significant because of the similarity in the results obtained using the different data sets and the exceptionally large temperature range.

The equilibrium constants, chemical-shift differences of diastereotopic groups, and coalescence temperatures of the other sulfenamides prepared were measured and are given in Table II. The rates of exchange and free energies of activation at the coalescence temperatures were obtained by interpolation using plots of k_c as a function of $\Delta\nu$ and K, derived from complete line-shape analyses. Assuming that the entropy of activation is the same for all of the sulfenamides investigated, enthalpies of activation and torsional rates at a common temperature (300°K) were calculated for comparison purposes. These data are also collected into Table II.

Discussion

As illustrated by the data in Table II, equilibrium constants and torsional barriers are affected by substituents at nitrogen and sulfur. The most pronounced effect on torsional barriers results from changes in the electron-withdrawing power of the substituent at sulfenyl sulfur. The barriers are highest when the group is strongly electron withdrawing. Thus, the trichloromethyl-, 2,4-dinitrophenyl-, and 2-nitrophenyl-substituted compounds exhibit higher torsional barriers than phenyl or *p*-tolyl derivatives. These trends are in accord with a contribution to the torsional barrier from overlap between the nitrogen lone-pair orbital and one of the sulfur d orbitals as discussed in an earlier paper in this series.[7] The small difference in the barriers in benzenesulfonyl and *p*-toluenesulfonyl derivatives **2a** and **2d** is likewise a reflection of electronic effects discussed previously.[7] Steric bulk also affects torsional barriers. Thus the 1-naphthyl compound **2g** has a higher barrier than the phenyl derivative **2a**.

In the absence of an additional asymmetric substituent, the two stereoisomers, (*R*)-**1** and (*S*)-**1**, would have the same free energy of formation. The presence of the asymmetric carbon atom perturbs the degeneracy in the energies of (*R*)-**1** and (*S*)-**1** and thereby induces a prefer-

Table III

T, °C	k, sec^{-1}
−65	0.000012 (±0.000007)
−58	0.000049 (±0.000001)
−53	0.000106 (±0.000002)
−48	0.00023 (±0.00003)
28	1.5
35	2.8
39	4.5
41	5.0
42	5.6
44	6.8
53	14
56	18
60	22
62	26
65	30
67	33
68	40
73	57
84	120
92	205

The sulfenamide system thus provides a case wherein the magnitude of asymmetric induction is determined by other than steric factors. One possible explanation for this phenomenon is related to the dependence of the torsional barrier on p–d π bonding and substituent electronegativity as discussed above. The increased electronegativity of the sulfenyl substituent imparts an increased measure of rigidity to the S–N bond because of a dependence of the magnitude of p–d π bonding on the dihedral angle. This increased rigidity may make the sulfenyl chiral unit more susceptible to asymmetric perturbation by the second chiral unit.

The negative entropy of activation measured for **2a** seems large for a simple unimolecular conformational change which does not involve bond making at the transition state. The negative sign of the entropy of activation indicates a considerable ordering of the transition state. The negative sign of the entropy of activation indicates a considerable ordering of the transition state (including its solvation shell) with respect to

Table IV

			Anal.					
			Calcd			Obsd		
Compd	Mol form	Mp, °C	C	H	N	C	H	N
2a	$C_{15}H_{14}NO_2S_2Cl_3$	85–86.0	43.86	3.44	3.41	44.08	3.63	3.43
2b	$C_{20}H_{19}NO_2S_2$	91–93	65.01	5.18	3.79	64.78	4.96	3.90
2c	$C_{21}H_{21}NO_2S_2$	85–86.5	65.77	5.52		65.71	5.76	
2d	$C_{16}H_{16}NO_2S_2Cl_3$	91.5–93	45.24	3.80	3.30	45.46	3.90	3.19
2e	$C_{21}H_{19}N_3O_6S_2$	134–136	53.27	4.04	8.87	53.47	4.18	8.84
2f	$C_{21}H_{20}N_2O_4S_2$	142.5–143.5	58.86	4.70	6.54	58.58	4.77	6.56
2g	$C_{19}H_{16}NO_2S_2Cl_3$	129–130	49.52	3.50	3.04	49.71	3.60	3.30

ence for a particular configuration. This phenomenon is an equilibrium analog to the asymmetric induction which occurs in asymmetric synthesis, wherein an existing chiral unit induces a preference for a particular configuration at a new chiral unit being formed. The absolute rate theory postulates that the magnitude of asymmetric induction in an asymmetric synthesis may be calculated by assuming an equilibrium between the two diasteromeric transition states which lead to stereoisomeric products. The true equilibrium between diastereomeric sulfenamides is analogous to the pseudo-equilibrium between diastereomeric transition states. While the ratio of stereoisomers formed in asymmetric synthesis is proportional to the exponential of the difference in free energies of activation, the ratio of mole fractions of epimeric sulfenamides is proportional to an exponential of the difference in free energies of formation. The equilibrium asymmetric induction in sulfenamides can thus serve as a useful model for asymmetric synthesis which has the advantage that the detailed structures of the diastereomeric entities can be studied directly rather than only indirectly.

In the present instance it is clear that steric bulk affects equilibrium constants as would be expected. The replacement of the phenyl group in the side chain of **2a** by the more bulky 1-naphthyl group increases the equilibrium constant considerably, probably because of an interaction involving the *peri* hydrogen.

More surprising is the apparent affect of electronegativity on the degree of asymmetric induction. Thus, the addition of a *p*-nitro group to the *o*-nitro phenyl ring of **2f** changes the equilibrium constant from 1.9 to 2.4. the ground state. Two possible contributors to the negative entropy of activation suggest themselves. First, the greater congestion in the transition state, as the trichloromethyl group eclipses one of the two nitrogen ligands, is expected to lead to a reduction in degrees of freedom for torsion about the bond to the eclipsed ligand. A second possibility is suggested by the effect of electronegative groups on the barriers. In the ground state, positive charge on sulfur is somewhat delocalized by overlap of a sulfur d orbital with the nitrogen lone pair. By contrast, in the transition state p–d π bonding is diminished and the concentration of charge at sulfur is increased. The consequent increased requirement for solvation at the transition state might be expected to lead to greater ordering of the solvation shell and a decrease in entropy.

Experimental Section

The nmr spectra were measured on a Varian A-60A spectrometer equipped with a Varian variable temperature probe using *ca.* 10–20% solutions. Temperatures were determined using methanol or ethylene glycol spectra as described in the Varian manual or using the Van Geet[13] calibration curves. Those in Tables II and III were obtained using the Varian calibration curves.

Theoretical spectra were generated by an IBM 360/65 computer and plotted on a Calcomp plotter using a program based on the solution to the exchange-modified Bloch equations. The determination of rates of exchange by complete line-shape analysis involved obtaining correspondence between experimental and theoretical spectra.

We have used extensions of two different definitions of the coalescence temperature that can be used to describe coalescing singlets: the lowest temperature at which the minimum between the coalescing signals has vanished (minimum definition) or the lowest tem-

perature at which there is only one inflection point on either side of the maximum (inflection definition). For cases in which the equilibrium constant is near one (**2a**, **2b**, **2c**, and **2d**) these two definitions refer to the same signal shape; however, when the populations differ greatly from one (**2e**, **2f**, and **2g**), the two definitions correspond to different signal shapes and coalescence temperatures. When the equilibrium constant was substantially different from one, we chose the minimum definition. Rate constants at coalescence (by either definition) were determined by a complete line-shape method, and hence the free energies of activation reported are independent of the definition used.

***N*-Alkyl-*N*-arenesulfonylsulfenamides (2).** The title compounds were prepared by reaction of the appropriate *N*-alkylsulfonamides with butyllithium followed by reaction with the appropriate sufenyl chlorides as previously described.[7] Physical properties and analytical data are given in Table IV.

Kinetic Measurements. The rate constants (Table III) used to determine the activation parameters for **2a** were obtained using two methods. The low-temperature (−65 to −48°) rate constants were determined by conventional kinetics of equilibration as previously described.[11] The high-temperature (28–92°) rate constants were obtained by complete line-shape analysis.

Mechanism of Direct Cis–Trans Photoisomerization of the Stilbenes. Solvent Viscosity and the Azulene Effect[1]

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Abstract: The azulene effect on cis–trans stationary states for direct stilbene photoisomerization is shown to be independent of solvent viscosity, while the azulene effect on the sensitized stilbene photoisomerization is shown to be viscosity dependent. The observations support the proposal that the azulene effect on the direct photoisomerization is due to long-range (~15 Å) radiationless excitation transfer from *trans*-stilbene singlets, whereas the azulene effect on the sensitized photoisomerization is due to diffusion-controlled excitation transfer from *trans*-stilbene triplets. Experiments in which Oil Yellow is used as the acceptor of stilbene excitation are similarly explained. It is concluded that intersystem crossing does not lie in the major path for direct stilbene photoisomerization. The unexpectedly large effect of azulene on the sensitized photoisomerization in *tert*-butyl alcohol is attributed to a ninefold increase of the effective lifetime of stilbene triplets in this solvent. The effect of azulene on the initial rates of benzophenone-sensitized *cis*-stilbene photoisomerization is found to be consistent with the proposed rapid conversion of cis triplets to trans triplets.

The studies of Dyck and McClure[3] and Malkin and Fischer[4,5] on the temperature dependence of the fluorescence quantum yield of *trans*-stilbene and trans → cis and cis → trans quantum yields of isomerization establish that almost all decay from the lowest excited singlet state of *trans*-stilbene, ^{1}t, can be accounted for by two processes: (1) fluorescence and (2) an activated crossing into the state from which isomerization takes place. Decay from cisoid excited singlets, ^{1}c, is practically temperature independent and leads almost exclusively to the state from which isomerization takes place. A marked drop in $\phi_{c\rightarrow t}$ at 77°K has been shown to be due mainly to increased medium rigidity and not to an internal barrier to rotation.[5,6] Study of the direct cis → trans photoisomerization is complicated by the fact that a small fraction, $\lesssim 0.1$, of ^{1}c molecules undergoes cyclization to dihydrophenanthrene.[7,8]

There has been much speculation concerning the identity of the state(s) involved in the cis → trans photoisomerization.[9] Most recently, the major question has concerned the identification of the activated process competing with *trans*-stilbene fluorescence. This process has been variously assigned to intersystem crossing into the triplet manifold (the triplet mechanism),[4-6,10] or to twisting about the central bond of the lowest excited singlet state (the singlet mechanism).[11]

Important in evaluating the triplet mechanism for stilbene photoisomerization have been studies involving the transfer of triplet excitation to the stilbenes from various triplets energy donors.[5,12,13] Such studies yield quantitative information concerning the behavior of stilbene triplets and allow comparison of the triplets with the intermediates obtained upon direct excitation. Most informative in this respect have been experiments in which azulene is employed as an excitation acceptor in both the direct and the sensitized isomerization of the stilbenes.[12] Inclusion of azulene leads to stilbene photostationary states which are richer in *trans*-stilbene, but the effect is much larger for the sensitized photoisomerization. It has been suggested, on the basis of scintillation counting experiments, that the azulene effect on the direct photoisomerization is due entirely to radiationless transfer of excitation from *trans*-stilbene sing-

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