Stereochemistry at Trivalent Nitrogen. VI. Slow Rotation about Nitrogen–Sulfur Formal Single Bonds in N,N-Dialkylsulfenamides[1-3]

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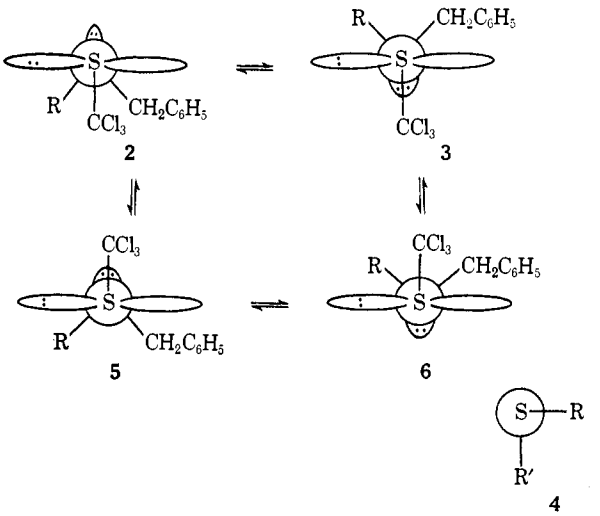
Abstract: Nuclear magnetic resonance chemical shift nonequivalence of diastereotopic protons in sulfenamides $R_1SNR_2R_3$ indicates that the ground-state conformation of these molecules is chiral. The coalescence of signals from diastereotopic nuclei accompanies a degenerate racemization reaction corresponding to two successive conformational changes, *viz.* inversion of the nitrogen pyramid and torsion about the sulfur–nitrogen bond. The energies of activation for the reaction were determined using nmr spectroscopy for the following compounds: N-alkyl-N-benzyltrichloromethanesulfenamides [$CCl_3SN(R)CH_2C_6H_5$, R = CH_3, CH_2CH_3, $CH(CH_3)_2$, 1-adamantyl, $CH_2C_6H_5$]; N-benzyl-2,4-dinitrobenzenesulfenamides [$2,4\text{-}(NO_2)_2C_6H_3SN(R)CH_2C_6H_5$, R = $CH(CH_3)_2$, C_6H_5]; N-benzyltrifluoromethanesulfenamides [$CF_3SN(R)CH_2C_6H_5$, R = CH_3, $CH(CH_3)_2$]; and N-trichloromethanesulfenyl-2,2-dimethylsuccinimide. Apparent chemical shift equivalence precluded the determination of barriers to conformational interchange in N-benzyl-N-isopropyl-*p*-toluenesulfenamide, N-benzyl-N-isopropylbenzenesulfenamide, and N-benzyl-N-phenyltrichloromethanesulfenamide. The steric and conjugative effects of the barrier provide evidence that the rate-determining step in the conformational interchange involves slow rotation about the sulfur–nitrogen formal single bond. The torsional barriers observed ranged from 12 to 18 kcal/mole.

At low temperatures the proton magnetic resonance spectra of N-alkyl-N-benzyltrichloromethanesulfenamides, $CCl_3SN(R)CH_2C_6H_5$ (**1**), exhibit AB quartets for the benzylmethylene hydrogens (Figures 1–4) signifying that these two hydrogens are diastereotopic, *i.e.*, that they reside in diastereomeric environments. This requires that the molecular geometry of these compounds be such that the symmetry plane (σ plane), which is present in many simple benzyl compounds such as benzyl chloride, be absent else the two hydrogen atoms would be enantiotopic and would have identical chemical shifts. Compounds in this series must have chiral geometries if the two alkyl groups on nitrogen differ.

Although the exact details of the conformation of these compounds are unknown, a plausible argument can be made in support of a conformation approximating one of those shown in Newman projection formulas **2** and **3**. We regard the nitrogen atom as pyramidal in consonance with the known conformation in amines. In suggesting that the CSNC dihedral angle is *ca.* 60° (**2**) or *ca.* 120° (**3**) we recall that the preferred conformation in disulfides is one in which the CSSC dihedral angle is *ca.* 90°.[4] This conformation (**4**) is one in which the two vicinal sulfur p orbitals are orthogonal (or nearly so) and the coulombic repulsion between the two nonbonded electron pairs in these orbitals is at a minimum. Although the relative importance of p–d π bonding and lone pair–lone pair repulsion in the maintenance of this geometry has been the subject of discussion,[4] it may be noted that a similar geometry exists in hydrogen peroxide where p–d π bonding cannot occur.[5] Similarly, the two hypothetical conformations, **2** and **3**, are ones in which the nodal surfaces of the nonbonded pair of electrons in the sulfur p orbital, and of the lone pair in the nitrogen sp^3 orbital, are approximately at a 90° angle and hence the geometry is one of minimum interaction between the two orbitals.[6]



The benzyl group is not the sole probe capable of making the dissymmetry of the sulfenamide grouping manifest in chemical shift nonequivalence of diastereotopic protons. The nmr spectrum (Figure 3) of N-ethyl-N-benzyltrichloromethanesulfenamide (**3c**) in chloroform at 0° features an AB quartet for the benzyl methylene protons and an ABX_3 system for the ethyl

(1) A portion of this work has appeared in preliminary form: M. Raban, F. B. Jones, Jr., and G. W. J. Kenney, Jr., *Tetrahedron Letters*, 5055 (1968).

(2) Part V: M. Raban and F. B. Jones, Jr., *J. Am. Chem. Soc.*, **91**, 2180 (1969).

(3) Supported in part by a Frederick Gardner Cottrell Grant-in-Aid from the Research Corporation, and a grant from the Petroleum Research Fund of the American Chemical Society (1139-G1). We are grateful for a generous grant of computing time from the Wayne State University Computing Center.

(4) O. Foss in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, Chapter 8, and papers cited therein.

(5) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261, 2276 (1967).

(6) This discussion is predicated on a model wherein the nitrogen atom is sp^3 hybridized but the sulfur is unhybridized and uses p orbitals for σ bonding. However, this model was chosen for convenience only and the conclusions would be substantially unchanged were a model with different hybridization at sulfur chosen.

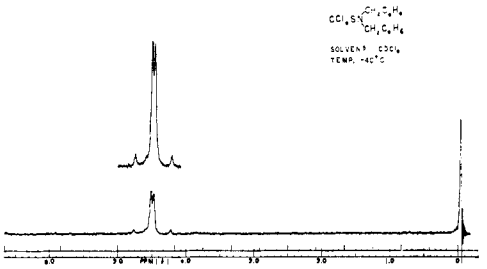
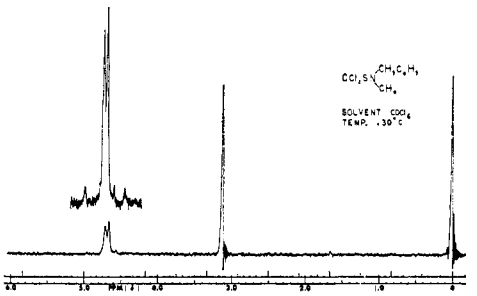


Figure 1.



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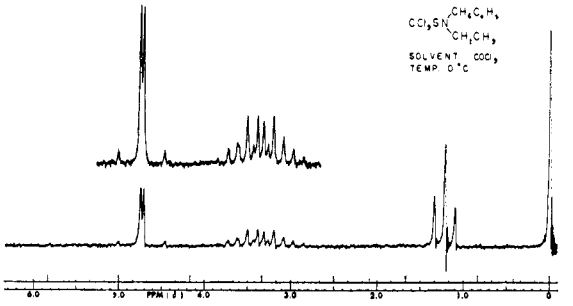


Figure 3.

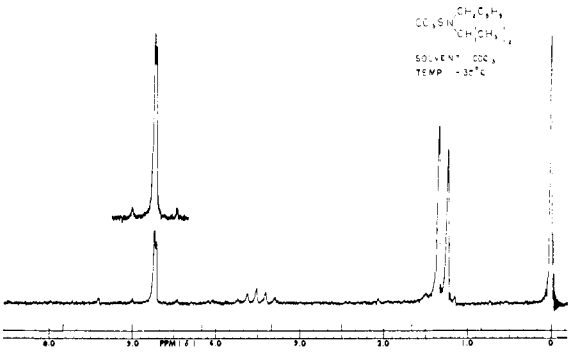
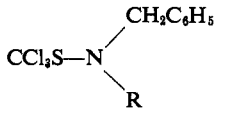


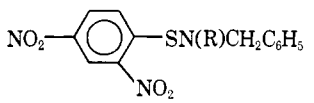
Figure 4.

group. It has been pointed out that although diastereotopic groups must in principle have different chemical shifts, this difference is not always large enough to be observable.[7] In such cases, we may speak of accidental equivalence or apparent equivalence. The nmr spectrum of **1d**, Figure 4, provides an example of this phenomenon. Although the diastereotopic benzyl methylene protons differ in chemical shift, only one isopropyl doublet is observed. By contrast the trifluoromethanesulfenamide, **8b**, exhibits observable nonequivalence of isopropyl methyl groups but not of the benzyl methylene protons. These examples illustrate vividly the caution required when evaluating the significance of apparent chemical shift equivalence.



1a, R = $CH_2C_6H_5$
b, R = CH_3
c, R = CH_2CH_3
d, R = $CH(CH_3)_2$
e, R = $C_{10}H_{15}$ (1-adamantyl)

Chemical shift nonequivalence was also observed for N-benzyl-N-isopropyl-2,4-dinitrobenzenesulfenamide (**7b**). However, N-benzyl-N-isopropyl-*p*-toluenesulfenamide (**9b**) and N-benzyl-N-isopropylbenzenesulfenamide (**9a**) exhibit chemical shift equivalence even at temperatures as low as −70°. Although we cannot rule out a situation like that discussed above, we do not believe, in this instance, that the apparent equivalence observed results from a difference in chemical shifts of diastereotopic groups which is too small to be measured. Rather, the equivalence of both the pair of isopropyl methyl groups and the pair of benzyl methylene protons implies to us that the averaged environments of the protons are enantiotopic within each set because of rapid conformational interchange.



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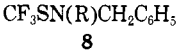

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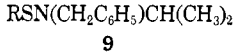

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When the nmr spectra of compounds **1** and **7** are taken at higher temperatures, the benzyl methylene AB quartets broaden, coalesce, and finally sharpen until at elevated temperatures sharp singlets are observed. This signals a conformational exchange, which is rapid on the nmr time scale, such that the averaged environments of the two benzyl methylene protons are no longer diastereotopic but enantiotopic. This conformational interchange corresponds to the rapid inversion of configuration, *i.e.*, racemization of each molecule (**2** ⇌ **6** or **3** ⇌ **5**). Since the bulk composition of the sample does not change we term this conformational change degenerate racemization.

Even though rapid racemization brings about the averaged identity of the chemical shifts of the two benzyl methylene hydrogens, these two hydrogens remain stereochemically distinguishable. This event can be visualized by labeling the two benzyl methylene protons according to the scheme proposed by Hanson.[8] The benzyl carbon atom is a prochiral carbon atom and we can label one of the benzyl methylene protons pro-*R* and the other pro-*S*. The proton labelled pro-*R* in **2** remains pro-*R* even after inversion of configuration (**2** ⇌ **6**) has taken place.

Thus it is not, strictly speaking, correct to say that the two protons are exchanged by the degenerate racemiza-

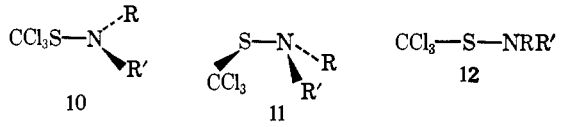
(7) K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. I, E. L. Eliel and N. L. Allinger, Ed., Interscience Publishers, New York, N. Y., 1967, Chapter 1.

(8) K. R. Hanson, *J. Am. Chem. Soc.*, **88**, 2731 (1966).

tion. Rather the environments of the two protons are diastereomeric in the absence of racemization, but the environments of the two protons averaged through the racemization are enantiomeric. When we say that conformational interchange results in coalescence and chemical shift equivalence, it is to be understood in this sense. However, since enantiotopic protons must have the same chemical shifts (in achiral solvents),[7] the maintenance of pro-*R* configuration is irrelevant to the coalescence of the signals of the two protons.

As illustrated, the degenerate racemization (**2** ⇌ **6** or **3** ⇌ **5**) involves two different conformational changes, inversion of the nitrogen pyramid (**2** ⇌ **3** and **5** ⇌ **6**) and the conformational change represented by **2** ⇌ **5** and **3** ⇌ **6**. This second conformational change can be effected by rotation around the sulfur–nitrogen bond or by inversion at sulfur. Although the final result of rotation around the N–S bond is identical with inversion at sulfur, the two processes have distinguishable transition states. We represent the three idealized transition states for nitrogen inversion, torsion, and sulfur inversion, **10**, **11**, and **12**, respectively.

Since the process of racemization and the coalescence which accompanies it involve two consecutive steps, we may suppose that two transition states and two activation energies are involved. Unless the two activation energies are of comparable magnitude, the Curtin–Hammett principle states that the transition state and activation energy of the overall reaction correspond to the higher energy transition state.



The free energy of activation for the racemization of N,N-dialkyltrichloromethanesulfenamides is of the order of magnitude of 15 kcal/mole. We may inquire whether any or all of the three hypothetical transition states **10**–**12** are likely to be greater in energy than the hypothetical ground state **2** or **3** by about this amount. Although little evidence is available concerning the energy required to invert a divalent sulfur atom, much work has been reported concerning the pyramidal stability of trivalent sulfur in sulfoxides and sulfonium salts.[9–11] If the energy of activation depends on the rehybridization of sulfur and the increased content of s character in the sulfur bonding orbitals, we might expect a similar or even higher barrier to the inversion of divalent sulfur since here, too, sulfur bonding orbitals which have preponderant p character in the ground state have greater s character in the transition state. The barriers for inversion of the sulfur pyramid range from 35 to 42 kcal/mole in diaryl sulfoxides[9] and are only somewhat lower (*ca.* 25 kcal/mole) in sulfonium salts,[10,11] in both cases substantially greater than the 12–17 kcal/mole observed for the racemization barrier in sulfenamides. If this analogy is valid we may reject inversion at sulfur as an element in the racemization mechanism. Experimental evidence supporting this conclusion is presented below.

By contrast, the inversion of the nitrogen pyramid in simple amines is known to be considerably more facile than the inversion at trivalent sulfur.[12] However, some examples of nitrogen inversion barriers which are substantial enough to give rise to chemical shift nonequivalence on the nmr time scale have been reported. These examples include compounds in which steric hindrance[13] or ring strain[14] inhibits inversion as well as compounds containing a heteroatom attached to nitrogen in which lone pair-lone pair repulsions are alleged to augment the inversion barrier.[15,16] Presumably, repulsion between the nitrogen lone pair of electrons and those of the heteroatom is greater when the nitrogen is hybridized sp^2 and the lone pair of electrons is in a p orbital than when the lone pair is in an sp^3 orbital. In one group of these compounds[15] in which both heteroatoms are part of a small ring or a fused ring system, torsion cannot occur and we do not have the problem of choosing between alternative conformational processes. Similarly, the hindered conformational change which gives rise to the nonequivalence and stereoisomerism of N-haloaziridines and N-haloazetidines must also be slow nitrogen inversion since a torsional barrier around the N–X bond is undefined. In the acyclic examples,[16] however, as in the sulfenamides, we cannot rule out the possibility that nitrogen inversion is rapid on the nmr time scale and that a torsional barrier is responsible for the nonequivalence and associated phenomena observed. The same arguments also pertain to the nonequivalence in sulfinamides,[17] aminophosphines,[18] and N,N,O-trialkylhydroxylamines,[19] in which torsional barriers have been used to explain nonequivalence. A theoretical study of the α-sulfinyl carbanion indicated that a torsional barrier was to be expected in that system[20] and has been confirmed experimentally.[21] Of particular relevance are the calculations carried out on methanethiol carbanion ($HSCS_2^-$).[22] These calcula-

(9) K. Mislow, *Rec. Chem. Progr.*, **28**, 217 (1967).
(10) D. Darwish, S. H. Hui, and R. Tomilson, *J. Am. Chem. Soc.*, 90, 5631 (1968).
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(12) G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Am. Chem. Soc.*, **89**, 3396 (1967).
(13) W. N. Speckamp, U. K. Pandit, P. K. Korver, P. J. van der Haak, and H. O. Huisman, *Tetrahedron*, 22, 2413 (1966).
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(16) (a) D. L. Griffith and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 4089 (1965); (b) R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, *J. Chem. Soc.*, 7203 (1965); (c) C. K. Murayama and T. Yoshioka, *Tetrahedron Letters*, 1363 (1968).
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(21) H. Kloosterziel, *Chem. Commun.*, 1330 (1968).

tions indicated that the ground state of this hypothetical ion is that corresponding to **2**. The diastereomeric conformation **3** was found to be less stable than **2** by 6.1 kcal/mole. It was found that inversion of the carbon atom (**5** → **6**) took place spontaneously with zero activation energy while a substantial energy of activation (18.8 kcal/mole) was required for torsion (**2** → **5**). The chief difference between the results of Rauk's calculations on $HSCH_2^-$ and the qualitative description given above for **1** is that the calculations indicated that the process corresponding to the degenerate racemization of **1** proceeds *via* a single transition state corresponding to a torsional barrier rather than *via* two successive transition states corresponding to inversion and torsion.

It might seem that the existence of substantial nitrogen inversion barriers due to the presence of an adjacent heteroatom in cyclic compounds provides a precedent for attributing chemical shift nonequivalence in the acyclic sulfenamides to slow inversion of the nitrogen pyramid. The application of this precedent to acyclic examples, however, may be invalid since the ground state geometries of the cyclic and acyclic systems differ significantly. The ground states for the cyclic and bicyclic systems referred to above have a CYNC (Y = heteroatom) dihedral angle near zero because of the constraint of the ring system. As we have pointed out, this geometry corresponds to the transition state for torsion and will involve a substantial interorbital repulsive interaction. It may well be that only in this geometry will inversion of the nitrogen pyramid through a planar sp^2 transition state provide a significant enough increase in interorbital repulsion to be manifest in a substantial inversion barrier.

Results and Discussion

Evidence is presented here, based on steric and conjugative effects, that the chemical shift nonequivalence and coalescence observed in the nmr spectra of sulfenamides is associated with a substantial torsional barrier rather than a barrier to nitrogen inversion. Comparison of the barriers to conformational interchange in acyclic sulfenamides with those in N-sulfenylaziridines and examination of the steric effect on the barrier have also been used to provide evidence in support of a torsional barrier[23] in accord with the results presented here.

Examination of conjugative and steric influences on the barrier can provide grounds for a choice between transition states **10** (nitrogen inversion), **11** (S–N torsion), and **12** (sulfur inversion) for the transition state of the slow step in the conformational interchange. The attachment of an unsaturated substituent to the nitrogen atom such as phenyl or carbonyl will change the hybridization at nitrogen by providing greater p character to the orbital of the nonbonded electrons to facilitate conjugation,[24] and hence to lower the inversion barrier appreciably.

Unfortunately, the first compound of this type investigated, **1**, R = C_6H_5, exhibited apparent chemical shift equivalence for the benzyl methylene protons not only at 0°, where nonequivalence was manifest in the spectra of the dialkyl members of the series (**1**, R = alkyl) but even at −70°, the lowest temperature at which the spectrum was recorded. This result might have been due either to a much lower inversion barrier or to apparent chemical shift equivalence. Fortunately, N-benzyl-N-(2,4-dinitrobenzenesulfenyl)aniline, 2,4-$(NO_2)_2C_6H_3SN(C_6H_5)CH_2C_6H_5$ (**7a**), does not exhibit the same behavior. In this compound, the trichloromethyl group has been replaced by the 2,4-dinitrophenyl group which is also highly electronegative and which produces substantial barriers to conformational interchange.[2,25] The nmr spectrum of **7a** in toluene-d_8 at room temperature exhibits chemical shift nonequivalence of diastereotopic benzyl protons. As the temperature in increased, the AB quartet, originally observed, broadens and collapses to a singlet which sharpens as the temperature is raised above the coalescence temperature (T_c = 78°). The rate at T_c was calculated using the expression of Kurland[26] and the free energy of activation was obtained from the Eyring equation (ΔG^* = 17.8 kcal/mole). An effort to obtain the rate constants corresponding to spectra taken at other temperatures was made by comparison of experimental spectra with theoretical spectra obtained using a computer program based on Alexander's density matrix equation for the intramolecular interchanging AB system.[27] Spectra calculated using as an estimate for $\Delta\nu_0$ the chemical shift difference obtained below the region of line broadening could not be made to correspond with experimental spectra. This change in chemical shift nonequivalence with temperature is a well-documented phenomenon. The total chemical shift difference between diastereotopic protons is the sum of two terms, $\Delta\nu_{cp}$ and $\Delta\nu_{id}$.[28] The latter, due to the *intrinsic diastereomerism* of the environments of the two protons, is independent of conformational equilibria and, hence, likely to be nearly invariant with respect to temperature. However, the former is dependent on *conformer* populations and, hence, is likely to be strongly dependent on temperature. The choice of $\Delta\nu_0$ at each temperature was made on the basis of best fit between experimental and theoretical spectra using a computer program which iterated both the rate and $\Delta\nu_0$. In this way, estimates of the rates over a range of temperatures were made and an Arrhenius plot afforded kinetic parameters: E_a = 24.8 ± 1.0 kcal/mole, log A = 17.3 ± 0.8, ΔH^* = 24.1 ± 1.0 kcal/mole, ΔS^* = 18 ± 3 eu. However, we believe that in situations like this, complete line shape analysis does not always furnish reliable estimates of entropy and enthalpy of activation and, as a consequence, we have relied on free energies of activation at the coalescence temperature in the remainder of this study.[29]

The free energy of activation found for **7a** is to be compared with that of N-benzyl-N-(2-propyl)-2,4-dinitrobenzenesulfenamide, **7b**, in which the phenyl group has been replaced by the nearly isosteric isopropyl group (Table I). If nitrogen inversion were the process

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(28) M. Raban, *Tetrahedron Letters*, 3105 (1966); G. Redl and G. J. D. Peddle, *J. Phys. Chem.*, 73, 1150 (1969), and papers cited therein.
(29) The direct equilibration method which was used to obtain kinetic parameters for a related sulfenamide[25] has indicated that the activation entropy for torsion is low in contrast to the results reported here (unpublished results).

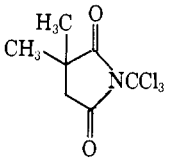
Table I. Nmr and Analytical Data

Compd no.	R	Solvent	$\Delta\nu$, Hz[a]	J_{AB}, Hz	T_c, °C	ΔG^*, kcal/mole	Calcd, % C	Calcd, % H	Calcd, % N	Obsd, % C	Obsd, % H	Obsd, % N
1a	$CH_2C_6H_5$	$CDCl_3$	9.0	14.8	27	14.9	51.95	4.06	4.04	51.91	4.08	4.43
1b	CH_3	$CDCl_3$	9.0	14.7	17	14.4	39.94	3.72	5.17	39.87	3.88	5.29
1c	CH_2CH_3	$CDCl_3$	8.7	14.8	40	15.6	42.19	4.25	4.92	42.47	4.47	5.12
1d	$CH(CH_3)_2$	$CDCl_3$	8.2	14.9	48	16.0	44.23	4.72	4.69	44.26	4.83	5.02
1e	$C_{10}H_{15}$ (1-adamantyl)	C_6H_5Br	20.9	15.9	68	16.9	55.31	5.68		54.84	5.81	
1f	C_6H_5	$C_6D_5CD_3$	*b*		*b*		50.53	3.63	4.21	50.77	3.81	4.56
7a	C_6H_5	$C_6D_5CD_3$	20.5	17.0	78	17.8	58.46	3.85	11.02	58.35	3.98	11.06
7b	$CH(CH_3)_2$	$C_6D_5CD_3$	5.9	13.9	57	16.5	55.44	4.90		55.68	5.04	
8a	CH_3	$CDCl_3$	*b*		*b*		48.85	4.59		48.99	4.82	
		$C_6D_5CD_3$	15.6	13.3	−35	11.8						
8b	$CH(CH_3)_2$	$CDCl_3$	2.9[c]		−30	13.3	52.99	5.66	5.62	53.10	5.86	5.66
		$C_6D_5CD_3$	11.0[c]		−13	13.5						
9a	C_6H_5	$CDCl_3$	*b*		*b*		74.70	7.39	5.45	74.43	7.59	5.65
9b	$C_6H_5CH_3$	$CDCl_3$	*b*		*b*		75.28	7.75		75.38	7.76	
13		$CDCl_3$	3.3[d]		−53	11.8	31.11	2.96	5.18	30.97	3.20	5.06

[a] Chemical shift differences refer to benzyl methylene protons except as indicated. [b] Chemical shift equivalent was observed down to −70°. [c] Chemical shift nonequivalence was observed only for the isopropyl group; the benzyl group appeared as a singlet even at low temperatures. [d] Geminal methyl groups. Nonequivalence was also observed for methylene protons.

observed, we would expect the barrier for the phenyl compound to be on the order of 8 kcal/mole lower, the difference in the barriers observed for N-cyclohexyl and N-phenylaziridines.[14c] On the contrary, the barrier observed for **7a** is somewhat higher than that of **7b**.

A more dramatic example is provided by 2,2-dimethyl-N-(trichloromethanesulfenyl)succinimide (**13**).



13

The effect of amide resonance in greatly lowering the barrier to nitrogen inversion is well known. Although the barriers to nitrogen inversion are known to be very high (*ca.* 20 kcal/mole) in N-alkylaziridines, replacement of the alkyl group by a carbonyl function drastically decreases the barrier. Thus, the free barriers in N-carbomethoxyaziridine and N-carbodimethylaminoaziridine are reported to be 7.6 and 10.8 kcal/mole, respectively, and the barrier in N-acetylaziridine, which could not be measured, is presumably even lower.[14c] X-Ray diffraction studies of a variety of amides, including the very closely related N-bissuccinimidyl,[30] have indicated that the amide nitrogen is planar within experimental error. Based on the above, we can be confident that the geometry of the nitrogen in **13** is either planar or very nearly planar and that the barrier to inversion, if one exists, can be no larger than a few kilocalories per mole at the most. The nmr spectrum of **13** does exhibit chemical shift nonequivalence of diastereotopic methylene and methyl signals. The energy of activation for racemization at the coalescence temperature for the two methyl singlets was calculated using the expression $k = \pi\Delta\nu/\sqrt{2}$,[31] and the Eyring equation: $\Delta\nu = 3.3$ Hz, $T_c = -53°$, $\Delta G^* = 11.8$ kcal/mole. Since we may exclude slow pyramidal inversion at nitrogen as the source of the nonequivalence in this compound, it is clear that a substantial torsional barrier exists about the S–N bond.

Further evidence that the rate-determining step in the degenerate racemization of the dialkyl compounds involves S–N torsion lies in the steric effect on the rate of reaction. The steric effect on pyramidal nitrogen inversion barriers has been documented in aziridines[14d] and oxazetidines.[15d] At the transition state for inversion, the C–N–C bond angles have expanded to *ca.* 120° from *ca.* 109° in the ground state. This expansion can remove or decrease congestion which occurs in the ground state when bulky groups are present. Consequently, a decrease in the barrier to nitrogen inversion (steric acceleration) is expected and has been observed[14d,15e] when the steric bulk of ligands attached to the nitrogen atom is increased. Similarly, inversion at sulfur is expected to occur with steric acceleration if any steric effect is observed.[9]

By contrast, in the transition state for torsion the C–S–N–C dihedral angle is smaller than in the ground state. Consequently, there should be more steric hindrance in the transition state if bulky groups are present. Thus, an increase in the torsional barrier (steric deceleration) may be anticipated upon increasing the steric bulk of substituents on nitrogen. Since the rate of the overall reaction is determined by the rate of the slow step, the steric effect can provide a diagnostic aid in the determination of the process involved in the rate-determining step.

A series of trichloromethanesulfenamides with ligands of increasing bulk (methyl, primary, secondary, tertiary) was examined to provide evidence on this point. The compounds (**1b–e**) were prepared by reaction of the appropriate N-alkylbenzylamine with trichloromethanesulfenyl chloride in benzene. The preparation of the *t*-alkyl member of the series occasioned some difficulty. Reaction of N-*t*-butylbenzylamine with sulfenyl chloride did not afford the desired sulfenamide. One possibility for the failure of the reaction might have been elimination to isobutylene. The 1-adamantyl group, however, can provide a *t*-alkyl substituent in which elimination to give olefin would violate Bredt's rule,[32]

(30) G. S. D. King, *J. Chem. Soc., B*, 1224 (1966).
(31) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 223.

and reaction of N-1-adamantylbenzylamine with trichloromethanesulfenyl chloride afforded the last member of the series. The temperature of coalescence of the benzyl methylene AB quartet was measured for each compound and the first-order rate constant for conformational interchange was calculated.

The trend observed upon increasing the size of the alkyl group is evident both in the coalescence temperature and in the free energies of activation: the compounds containing bulkier groups racemize more slowly (Table I). This effect is also evident, though less marked, in the data for compounds **8** where the trichloromethyl group has been replaced by the less bulky trifluoromethyl group. We cannot be sure whether the increase in activation free energy reflects changes in activation enthalpies or entropies or both. In either event, the results point to a greater congestion in the transition state, which is more compatible with a torsional barrier than a barrier to inversion and in accord with the model of the methanethiol carbanion derived from theoretical calculations.[22]

Although the steric and conjugative effects on the barrier to conformational interchange indicate that the slow step involves a torsional barrier, they do not provide insight into the origins of this exceptional rotational barrier. We may consider as contributions to the barrier both effects which stabilize the ground state as well as those which destabilize the transition state. Steric hindrance provides one contributor to the destabilization of the transition state as indicated by the steric effect on the barrier. This contribution to the barrier is probably not substantial in the first member of the series (**1b**) and the substantial barrier observed for that compound implies that other contributors must be more important. Destabilization of the transition state can also be expected to result from coulombic repulsion between the lone pairs of electrons on sulfur and nitrogen as in disulfides and peroxides. In the ground state, the nodal plane of the sulfur lone pair is approximately at right angles to that of the lone pair on nitrogen minimizing this repulsive interaction. In the transition state, the local symmetry axes of the orbitals lie in the same plane or nearly so and the interorbital repulsion is at a maximum. The observation of chemical shift nonequivalence for sulfenamides bearing the trichloromethyl, trifluoromethyl, or 2,4-dinitrophenyl groups on sulfur but not for those with phenyl or *p*-tolyl substituents does not appear to be related to steric factors. Rather these results imply that a highly electronegative group on sulfur increases the barrier to S–N torsion. This result does not seem related to electron repulsion since electron withdrawal from sulfur would be expected to lead to decreased electron repulsion in the transition state. Although these electronic effects and those observed for N-alkyl-N-(arenesulfenyl)arenesulfonamides[2,25] as well as theoretical calculations[20,22] imply that additional factors must be involved, it would seem that interaction between lone pairs of electrons is a major factor responsible for torsional barriers about single bonds between atoms bearing nonbonded valence electrons in this and related systems.

Experimental Section

Elemental analyses were performed by Midwest Microlab, Inc. Nuclear magnetic resonance spectra were measured on a Varian A60-A spectrometer. Chemical shifts are reported in parts per million on the δ scale and refer to 10–20% solutions (w/v). Chemical shift differences between diastereotopic protons are reported in hertz. Temperatures were calibrated with methanol or ethylene glycol spectra as described in the Varian users manual. Melting points were measured on a Thomas–Hoover melting point apparatus. Secondary amines, except where indicated, trichloromethanesulfenyl chloride, and trifluoromethanesulfenyl chloride were obtained commercially and used without prior purification. Two arene sulfenyl chlorides were prepared by chlorination of the appropriate thiophenols:[33] benzenesulfenyl chloride, bp 55° (1 mm) (lit.[34] bp 58° (3 mm)); *p*-toluenesulfenyl chloride, bp 64–66° (0.5 mm) (lit.[34] bp 77.5–78.5° (2.5 mm)). 2,4-Dinitrobenzenesulfenyl chloride was prepared by treating benzyl 2,4-dinitrophenylsulfide with sulfuryl chloride,[35] mp 94–96° (lit.[35] mp 95–96°).

N-Alkyl-N-benzyltrichloromethanesulfenamides (1a–1d). A solution of trichloromethanesulfenyl chloride (perchloromethyl mercaptan) (0.05 mole) was added dropwise with stirring to a benzene (75 ml) solution of the appropriate secondary amine (0.10 mole). After the reaction mixture had been allowed to stir overnight, the precipitated amine hydrochloride was removed by filtration. The filtrate was washed successively with water, 10% aqueous sulfuric acid, water, 10% aqueous sodium bicarbonate, and water, dried with anhydrous magnesium sulfate, and solvent removed *in vacuo*. Column chromatography on alumina (benzene eluent) or Kugelrohr distillation afforded the desired products: **1b**, bp 140° (1.5 mm); **1c**, bp 130° (1.0 mm); **1d**, bp 120° (0.6 mm).

1-(N-Benzylideneamino)adamantane (14). A solution of adamantylamine hydrochloride (37.4 g, 0.2 mole) in 150 ml of water was made alkaline with 100 ml of 10% aqueous sodium hydroxide and extracted thrice with 30-ml protons of toluene. Benzaldehyde (40.2 g, 0.38 mole) was added to the combined dried toluene extracts and the solution refluxed for 5 hr using a Dean–Stark trap to remove the water formed (3.5 ml). The solvent and excess benzaldehyde were removed *in vacuo* and the product was recrystallized three times from methanol at −15°, mp 59.5–61° (lit.[36] mp 58.4–60°).

1-(Benzylamino)adamantane (14). A solution of imine **13** (10 g, 0.04 mole) in dry ether was added to an ethereal slurry of lithium aluminum hydride (1.5 g, 0.16 mole). The mixture was stirred for 28 hr in an atmosphere of dry nitrogen and the excess lithium aluminum hydride decomposed with ethyl acetate. The reaction mixture was partitioned between water and ether, the ethereal layer dried, and the solvent removed *in vacuo*. Distillation yielded 9.5 g (94% of theory) of the desired product, n^{25}D 1.5556 (lit.[36] n^{25}D 1.5548).

Anal. Calcd for $C_{17}H_{23}N$: C, 84.59; H, 9.60; N, 5.80. Found: C, 84.31; H, 9.58; N, 5.75.

N-(1-Adamantyl)-N-benzyltrichloromethanesulfenamide (1e). Trichloromethanesulfenyl chloride (3.86 g, 0.02 mole) was added dropwise to a solution of amine **14** (5.0 g, 0.02 mole), and triethylamine (3.00 g, 0.03 mole) in 150 ml of benzene and the reaction mixture stirred for 20 hr. The solution was filtered and the filtrate washed successively with water, dilute sulfuric acid, water, dilute aqueous sodium bicarbonate, water. The removal of solvent afforded a brown gum which could be only partially purified by chromatography on silica gel (tetrahydrofuran eluent). The chromatographed product exhibited the expected nmr spectrum (CCl_4, 20%, room temperature, δ units): 1.63; 2.02–2.18, multiplet, 15 H (adamantyl protons); 4.82, AB quartet, $\Delta\nu$ = 21 Hz, J = 16 Hz, 2 H (benzyl methylene); 7.23, singlet, 5 H (phenyl protons).

N-Benzyl-2,4-dinitrobenzenesulfenamides (7). A solution of 2,4-dinitrobenzenesulfenyl chloride (0.1 mole) in 50 ml of benzene was added dropwise to a solution of the appropriate secondary amine (0.2 mole) in 75 ml of benzene. The reaction mixture was stirred for 20 hr and the precipitated amine hydrochloride removed by filtration. The filtrate was washed with water, 10% aqueous sulfuric acid, 10% sodium bicarbonate, and water, dried with anhydrous magnesium sulfate, and concentrated to *ca.* 50 ml *in vacuo*. The concentrate was cooled and the precipitate was recrystallized from methanol: N-benzyl-N-isopropyl-2,4-dinitrobenzenesulfenamide

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(mp 116–118°, 53% yield); N-benzyl-N-phenyl-2,4-dinitrobenzenesulfenamide (mp 134–136°, 75% yield).

N-Benzyltrifluoromethanesulfenamides (8). A cooled solution (−10°) of trifluoromethanesulfenyl chloride (0.016 mole) in toluene was added with stirring to a cooled toluene solution (−10°) of the appropriate amine (0.032 mole) in a flask equipped with a Dry Ice filled cold finger condenser. After stirring for 4 hr at −10°, the solution was allowed to warm to room temperature and stirred for an additional 20 hr. The amine hydrochloride was filtered, the filtrate successively washed with water, 10% aqueous sulfuric acid, 10% aqueous sodium bicarbonate water, and dried over magnesium sulfate. The solvent was removed *in vacuo* and the product distilled (**8a**, bp 46° (0.3 mm); **9b**, bp 119–120° (20 mm), $n^{24}D$ 1.4738).

N-Trichloromethanesulfenyl-2,2-dimethylsuccinimide (13). A hexane solution of *n*-butyllithium (4.1 ml of a 23% solution) was added to a solution of 2,2-dimethylsuccinimide[37] (2.0 g, 0.15 mole) in 50 ml of dry dioxane. After stirring for an additional 30 min, a dioxane solution of trichloromethane-sulfenyl chloride was added dropwise. The reaction mixture was stirred for 20 hr, filtered, and the solvent evaporated *in vacuo*. Recrystallization from methanol afforded pure sulfenamide, mp 104–106°, yield 30%.

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Internal Rotation in Olefins. I. Kinetic Investigation by Nuclear Magnetic Resonance

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Abstract: Two rotational processes which occur in the compounds listed in Table I have been detected and investigated by nmr spectroscopy. The first one was identified as a "low-energy" rotation about the carbon–carbon double bond (ΔG^* = 9.1–19.4 kcal/mol), while the second as "high-energy" rotation about the nitrogen-to-sp^2 carbon bond (ΔG^* = 8.7–13.3 kcal/mol). The above two processes which occur within a single molecule were found to be independent of each other. For most of the compounds, the rates under consideration are within nmr time scale. Activation parameters were determined from variable temperature nmr studies. Barriers for rotation about the carbon–carbon double bond are sensitive to structural variations. The relationship between structural parameters and activation energies was studied.

It has been frequently stated[2] that the rotation about a double bond is restricted. Such a restriction, generally referred to room-temperature measurements, is a consequence of the high activation energy (25–65 kcal/mol) for the thermal isomerization of olefins.[3] The phenomenological consequence of this situation is, of course, the thermal stability of olefins. This is usually allowed to contrast with the "free" rotation at room temperature about single bonds, which is associated with low activation energies, starting from *ca.* 1 kcal/mol[4] and extending to well over 20 kcal/mol.[5] The result of such a situation is the extremely low thermal stability of conformers and moderate stability of atropo isomers at room temperature. The above activation-energy ranges for rotation about formal single and double bonds approach, and in many cases actually overlap, each other. There are well-known examples of rotational processes about single bonds with relatively high energy barriers, exceeding 20 kcal/mol. These, among others, are the well-documented atropoisomerism phenomenon of biphenyls,[5] and the recent isolation of stable rotational isomers of amides.[6] On the other hand, systems which undergo thermal rotation about a carbon–carbon double bond at room temperature and even well below it ($\Delta G^* < 20$ kcal/mol) are rare.[7] Furthermore, no systematic studies of structure–reactivity relationship or of the mechanism of rotation are available.

In a previous investigation[8] we have measured by nmr the free energy of activation for rotation about a C=C bond in several conjugated enamines, and found values lower than 13 kcal/mol. Such low energy barriers preclude, of course, the isolation of stable stereoisomers (*cis* and *trans* isomers) at room temperature. However, the rotational rates are within nmr time scale, and can be conveniently measured by this technique. Consequently, such a system of olefins, equilibrating at room temperature, provides an excellent substrate to study the relationship between structural parameters and kinetic effects of the isomerization process. Furthermore, a study of these systems may also shed light on the mechanism of the rotational process, which may conceivably proceed *via* a biradical or dipolar transition state. The factors which govern the activation energy for rotation about bonds are manifold. The bond order is only one such factor, while steric interactions are by no means less important. In addition, the evaluation

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