5-ml flask which was then filled to the mark. The CCl$_4$ solution was examined in a 1-mm BaF$_2$ cell with a Perkin-Elmer ir spectrophotometer for the intensity of the band at 1090 cm^{-1}.

Rate of Racemization (k_r). About 1.5 g of optically active sulfoxide of known specific activity was dissolved in 25 ml of thermostated aqueous perchloric acid. Two or three aliquots were withdrawn at various times, diluted with water, neutralized, and extracted with chloroform. The residual obtained from distillation under reduced pressure of the solvent was chromatographed on silica and eluent petroleum ether–ethyl ether (1:1). The specific activity of the recovered sulfoxide was measured polarimetrically.

Acknowledgments. We thank Dr. Milla Sedea Andreuzzi and Mr. Mario Tescari, Istituto di Chimica Analitica, Universita' Padova, for the mass spectra run on the CNR instrument Hitachi Perkin-Elmer RMU-6D.

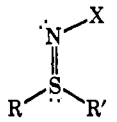
Cyclic Sulfimides and Sulfoximides

Joseph B. Lambert,*[1a] Craig E. Mixan,[1b] and David S. Bailey

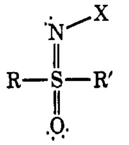
Contribution from the Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60201. *Received March 30, 1971*

Abstract: Thian-1-imide (**3**) has been synthesized and found to have a slight excess (55/45 at −85°) of the imide functionality in the equatorial position, in contrast to the isoelectronic thiane 1-oxide (**9**), which favors an axial orientation of the oxide functionality. The *N*-tosyl- (**6**) and *N*-benzenesulfonyl (**7**) derivatives of **3**, however, favor the axial imide conformation. Configurational criteria for the imide functionality on sulfur are developed on the basis of the chemical-shift difference and the coupling constant between the α protons. The resonances of the α or γ protons in these compounds (β positions deuterated) change from one averaged AB spectrum at room temperature to two distinct AB spectra at −90°, corresponding to the axial and equatorial imide conformers. The equilibrium constants are obtained directly from the spectra. Complete line-shape analyses of the spectral changes have produced activation parameters for ring reversal in thian-1-imide (**3**), thian-1-(*N*-tosyl)imide (**6**), thian-1-imide 1-oxide (**5**), and thian-1-(*N*-tosyl)imide 1-oxide (**8**).

The sulfimide[2] functional class **1** is the isoelectronic nitrogen analog of sulfoxides. The sulfur atom is pyramidal, with two aliphatic or aromatic substituents, one nonbonding electron pair, and the imide functionality. The S–N bond probably possesses some double-bond character due to (p–d)$_\pi$ bonding, but to a lesser extent than the S–O bond in sulfoxides. The sulfoximide class **2** bears a similar relationship to sulfones. In recent years there has been considerable effort in developing new preparative methods for these functionalities and in defining the stereochemistry of their reactions at sulfur.[3] In this paper we report the fundamental conformational properties of the sulfimide and sulfoximide functionalities incorporated into a six-membered ring.



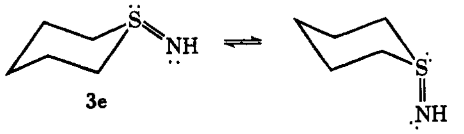
1



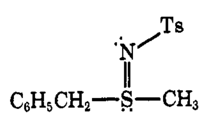
$$R-\underset{\underset{\textstyle \ddot{O}}{\|}}{\overset{\overset{\textstyle \dot{N}-X}{\|}}{S}}-R'$$

2

Three limiting conformational modes of interconversion are available to thian-1-imide (**3**) and its derivatives. (1) Ring reversal equilibrates the axial and equatorial forms (eq 1). The equilibrium constant is determined by the various interactions of the imide group with the rest of the molecule, and the activation energy to reversal depends on the torsional properties of the ring bonds. The nmr spectrum should be sensitive to this process,[4] with the room-temperature spectrum a weighted average for the two conformers and the low-temperature spectrum a set of discrete resonances for each. (2) Pyramidal inversion about sulfur should be slow on the nmr time scale.[3,5] This process therefore need not be considered in interpreting any temperature variation in the spectrum. To make certain that sulfur inversion is indeed slow, we examined *N*-tosylbenzylmethylsulfimide (**4**). Slow inversion is



3e **3a** (1)



$$C_6H_5CH_2-\overset{\overset{\textstyle \dot{N}-Ts}{\|}}{\underset{\cdot\cdot}{S}}-CH_3$$

4

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(1) (a) This work was supported by the National Science Foundation (Grants GP-9257 and GP-22942), the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center, and the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 2970-AC4,5); (b) National Science Foundation Trainee, 1968–1969.

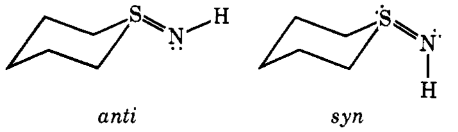
(2) Sulfimides are also referred to as sulfilimines or iminosulfuranes. The sulfoximides are frequently called sulfoximines; see P. E. Verkade, *Pure Appl. Chem.*, **11**, 158 (1965).

(3) D. J. Cram, J. Day, D. R. Rayner, D. M. von Schriltz, D. J. Duchamp, and D. C. Garwood, *J. Amer. Chem. Soc.*, **92**, 7369 (1970); C. R. Johnson and J. J. Rigau, *J. Org. Chem.*, **33**, 4340 (1968); M. A. Sabol, R. W. Davenport, and K. K. Andersen, *Tetrahedron Lett.*, 2159 (1968); K. Tsujihara, N. Furukawa, and S. Oae, *Bull. Chem. Soc. Jap.*, **43**, 2153 (1970); K. Tsujihara, T. Aida, N. Furukawa, and S. Oae, *Tetrahedron Lett.*, 3415 (1970), and other references in these.

(4) (a) J. B. Lambert and R. G. Keske, *J. Org. Chem.*, **31**, 3429 (1966); (b) J. B. Lambert, R. G. Keske, and D. K. Weary, *J. Amer. Chem. Soc.*, **89**, 5921 (1967).

(5) J. B. Lambert, *Top. Stereochem.*, **6**, 19 (1971); A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970).

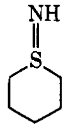
ensured by the fact that the methylene protons remain diastereotopic up to the limit of observation (+120°) in biphenyl. (3) If rotation about the S–N bond (or its functional equivalent, planar nitrogen inversion) is fast on the nmr time scale, this process may also be disregarded. The S–N bond order is probably quite low, but the question has not been fully explored as yet. Two situations are possible if rotation (and planar inversion) were slow. If the substituent on nitrogen lies on the plane that passes through N, S, and C-4 in **3**, slow rotation can only be distinguished if two isomers are present and give distinct resonances, *e.g.*, *syn*-**3e** and *anti*-**3e**. On the other hand, any equilibrium position of the N substituent off this plane at slow rotation destroys the equivalence of the α protons on either side of the ring, thereby doubling the number of α resonances for each conformer, **3e** and **3a**. Because spectral doubling of neither sort was observed (*vide post*), the S–N rotation process must be fast on the nmr time scale.



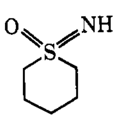
anti *syn*

3e

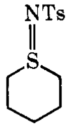
Similar processes of ring reversal and N–S rotation may be considered in studying the nmr spectra of thian-1-imide 1-oxide (**5**) and its derivatives. By examination of the spectral changes with temperature for the sulfimide **3** and its *N*-sulfonyl derivatives **6** (tosyl) and **7** (benzenesulfonyl), and for the sulfoximide **5** and its *N*-tosyl derivative **8**, it has been possible to evaluate the energetics of ring reversal and to determine the conformational preference of the imide group on sulfur.



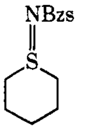
3



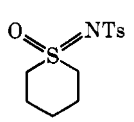
5



6



7

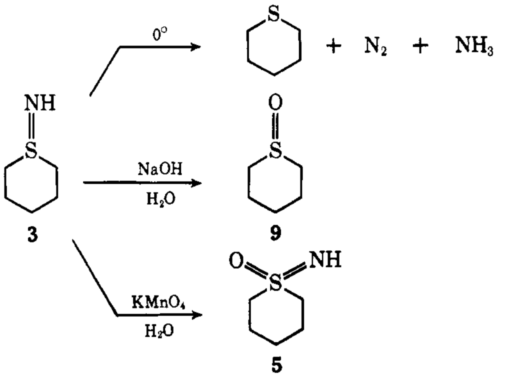


8

Results

All compounds in this study were derived ultimately from thiane, which had been fully deuterated in the β positions in order that the α and γ-resonances be free of vicinal couplings.[4a] The *N*-tosyl (**6**) and *N*-benzenesulfonyl (**7**) derivatives were obtained directly from thiane by treatment with chloramine-T (ClNHTs) and chloramine-B, respectively.[3] The sulfoximide **5** was obtained by treatment of thiane 1-oxide (**9**)[4a] with sodium azide according to the method of Johnson and Rigau.[3] Treatment of **5** with tosyl chloride produced the *N*-tosylsulfoximide **8**. Alternatively, **8** was obtained by the reaction of **6** with potassium permanganate.

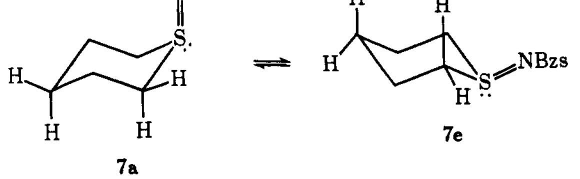
The method of Appel and Büchner[6] for the preparation of diethylsulfimide was used to synthesize thian-1-imide (**3**). Thiane was allowed to react with hydroxylamine-*O*-sulfonic acid (H_2NOSO_3H) to form the sulfimidium salt, which was decomposed to **3** by treatment with ammonia. The structure was confirmed by its nmr spectrum (*vide infra*) and by its reactions. The material disproportionates to thiane, ammonia, and nitrogen above −30°. Hydrolysis with sodium hydroxide produces the known thiane 1-oxide (**9**). Treatment with potassium permanganate yields thian-1-imide 1-oxide (**5**). These reactions, which are characteristic of the sulfimide functional class,[6] are summarized in eq 2.



(2)

At room temperature the nmr spectra of **3** and **5**–**8** are averaged by ring reversal, so that separate resonances for the axial and equatorial imide isomers are not observed. This process does not bring a geminal pair of protons into equivalence, since sulfur inversion is slow. A proton cis to the imide group remains cis after ring reversal; there is no configurational change, only a conformational one. Thus, the α (or γ) protons give an AB spectrum at room temperature, unless there is accidental equivalence. For the one example so examined, **6**, this AB nonequivalence persists to above 150°. As the temperature is lowered, the α (or γ) resonances pass reversibly through a coalescence and ultimately produce two AB spectra at the slow-exchange limit. One AB spectrum derives from the axial imide isomer, the other from the equatorial imide isomer.

Figure 1 displays the spectrum of the γ protons of thian-1-(*N*-benzenesulfonyl)imide (**7**) in $CHClF_2$ at the high- (27°) and low-temperature (−89°) extremes. At −89°, two AB spectra are clearly evident. The lower intensity AB quartet centered at higher field (peaks 2, 4, 6, and 8 from left to right) is assigned to the equatorial imide isomer (see Discussion). Ring reversal (eq 3) necessarily averages the resonance of an equatorial proton in one isomer with that of an axial proton in the other. Thus, peaks 1 and 3 (equatorial proton of **7a**) average with 6 and 8 (axial proton of **7e**), and peaks 2 and 4 (equatorial proton of **7e**) with 5 and 7 (axial proton of **7a**). This "crossover averaging" produces a high-temperature spectrum with a small chemical-shift difference. So long as the axial proton resonates at higher field in both isomers, crossover averaging must occur.[4a]



7a

(3)

Such a crossover was observed for the γ protons in all four compounds (**3**, **6**–**8**), and for the α protons except those in the parent imide **3**. Figure 2 displays the

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(6) R. Appel and W. Büchner, *Chem. Ber.*, **95**, 849, 855 (1962).

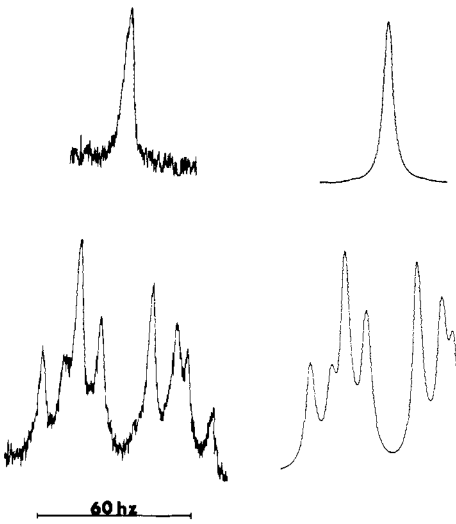

Figure 1. The fast-exchange (27°, upper) and slow-exchange (−89°) 90-MHz spectra of the γ protons of thiane-*3,3,5,5-d*$_4$-1-(*N*-benzenesulfonyl)imide (**7**) in $CHClF_2$. The more intense AB spectrum (peaks 1, 3, 5, 7) corresponds to the axial imide isomer.

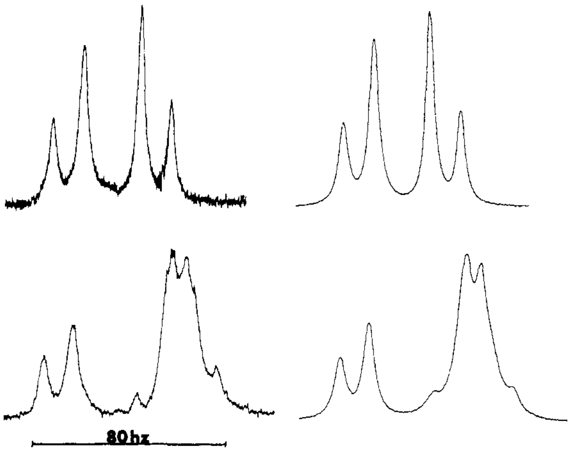

Figure 2. The fast-exchange (−30°, upper) and slow-exchange (−85°) 90-MHz spectra of the α protons of thian-*3,3,5,5-d*$_4$-1-imide (**3**) in 1:1 $CHClF_2$–CH_2Cl_2. The AB spectrum with the larger chemical-shift difference comes from the equatorial imide isomer; the AB spectrum of the axial isomer has a small chemical-shift difference and falls on top of the higher field doublet of **3e**.

high- (−30°) and low-temperature (−85°) spectra for the α protons of **3** in $CHClF_2$–CH_2Cl_2. At −85°, the resonances of the higher field AB quartet (the axial isomer, **3a**) are superimposed on the high-field half of the quartet centered at lower field (**3e**). A fit of the −30° spectrum from the −85° parameters requires that there be no crossover averaging. Therefore, in one isomer (axial imide, *vide post*) the axial proton resonates unexpectedly at lower field than the equatorial proton. The absence of crossover averaging produces a relatively large chemical-shift difference for the high-temperature extreme.

The entire temperature range of spectral changes for the γ protons of thian-1-imide in $CHClF_2$–CH_2Cl_2 is given in Figure 3. At −85°, peaks 1, 3, 6, and 7 come from the less populous isomer **3a** (see Discussion), and 2, 4, 5, and 6 from **3e** (peak 6 is an overlap of one resonance from each isomer). Rates were determined at each temperature by a complete line-shape analysis.[4a]

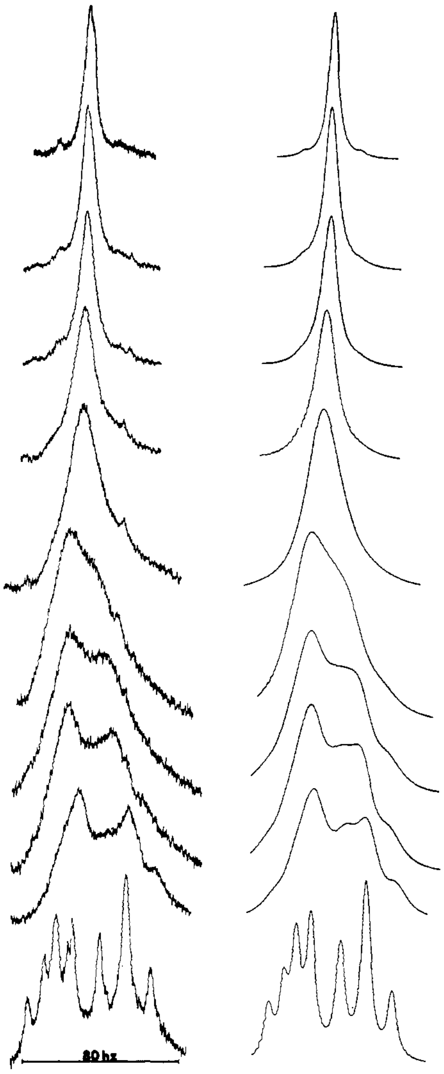

Figure 3. The observed (left) and calculated 90-MHz spectra of the γ protons of thian-*3,3,5,5-d*$_4$-1-imide (**3**) in 1:1 $CHClF_2$–CH_2Cl_2 as a function of temperature. There is a small impurity peak on the right side of the observed spectra. From top to bottom, the temperatures and the mean lifetimes (k^{-1} in seconds) for both isomers are −30 (fast exchange), −41 (0.0010, 0.0012), −45 (0.0016, 0.00195), −50 (0.0030, 0.0037), −54.5 (0.0062, 0.0076), −59 (0.0135, 0.0165), −61.5 (0.020, 0.0245), −63 (0.024, 0.029), −65 (0.030, 0.037), and −85 (slow exchange). At −85°, peaks 1, 3, 6, and 7 come from the axial imide isomer.

The complicated changes in the spectra yield relatively accurate rate constants.[7]

The observed and calculated spectra for the γ protons of thian-1-(*N*-tosyl)imide (**6**) in $CHClF_2$ are given in Figure 4. Normal crossover averaging occurs to give a high-temperature average with a small chemical-shift difference. At −80°, peaks 2, 4, 6, and 8 correspond to the higher field, less populous equatorial isomer **6e**. The spectra for thian-1-(*N*-benzenesulfonyl)-imide (**7**) were quite similar to those for **6** and are not reproduced.

The spectra for the α protons of the *N*-tosylsulfoximide **8** in $CHClF_2$ are given in Figure 5. Peaks 1, 2, 5, and 6 correspond to the more populous isomer, and peaks 2, 3, 4, and 5 to the less populous isomer (peaks 2 and 5 are an overlap of resonances from both forms).

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[7] D. A. Kleier, G. Binsch, A. Steigel, and J. Sauer, *J. Amer. Chem. Soc.*, **92**, 3787 (1970).

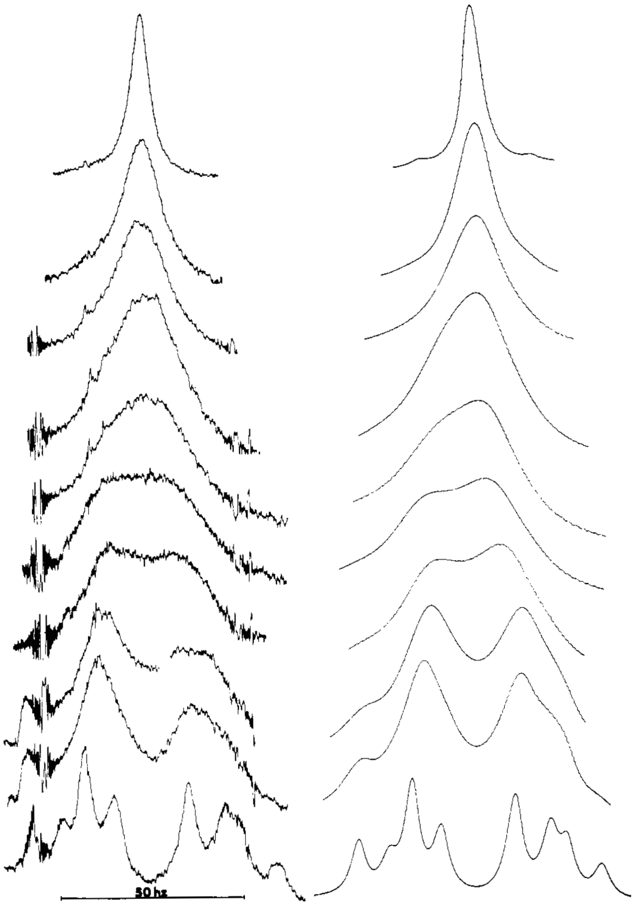

Figure 4. The observed (left) and calculated 90-MHz spectra of the γ protons of thiane-*3,3,5,5-d_4*-1-(*N*-tosyl)imide (**6**) in $CHClF_2$ as a function of temperature. The beat pattern at the left side of the observed spectra is entirely instrumental. From top to bottom, the temperatures and the mean lifetimes (k^{-1} in seconds) for both isomers are -30 (fast exchange), -49.5 (0.0036, 0.0024), -52 (0.0060, 0.0040), -55 (0.0093, 0.0062), -56.5 (0.0113, 0.0075), -58 (0.0149, 0.0099), -60 (0.0165, 0.011), -62.5 (0.030, 0.020), -65.5 (0.045, 0.030), and -80 (slow exchange). At $-80°$, the more intense peaks 1, 3, 5, and 7 correspond to the axial imide isomer.

Interestingly, the centers of the two AB quartets precisely coincide, giving the spectra an accidental mirror symmetry.

Only one AB quartet is observed at low temperature for the γ protons of the sulfoximide **5** in CH_2Cl_2. Either only one isomer is present, or the two AB quartets are exactly superimposed. Because the spectral temperature dependence resembles the well-known A_2 to AB change, a figure is omitted. Rates were determined by the complete line-shape method.

The spectral data obtained from the low-temperature extremes of **3** and **5**–**8** are given in Table I. These include the chemical-shift differences, the coupling constants, and the populations for both isomers. All three types of parameters were allowed to vary to obtain the best fit of the slow- and fast-exchange spectra. For comparison, the data for thiane 1-oxide (**9**)[4a] are included. All parameters are probably accurate to ± 0.2 Hz. The mean lifetimes (k^{-1}) for ring reversal are given in the captions for the figures. Table II presents the activation parameters calculated from the rate constants.

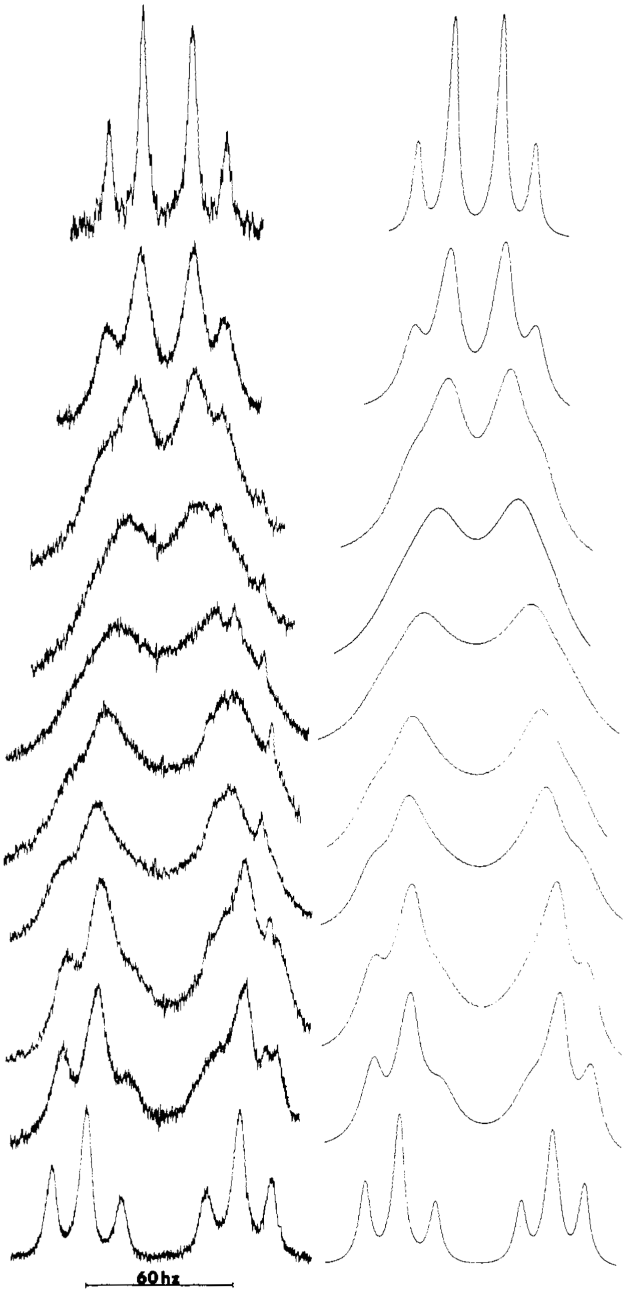

Figure 5. The observed (left) and calculated 90-MHz spectra of the α protons of thiane-*3,3,5,5-d_4*-1-(*N*-tosyl)imide 1-oxide (**8**) in $CHClF_2$ as a function of temperature. There is a small impurity peak at the extreme right of the observed spectra. From top to bottom, the temperatures and the mean lifetimes (k^{-1} in seconds) for both isomers are $+27$ (fast exchange), -45 (0.00165, 0.00085), -51 (0.0039, 0.0020), -54 (0.0070, 0.0036), -58 (0.0110, 0.0057), -62 (0.0175, 0.0089), -65 (0.024, 0.0120), -67.5 (0.038, 0.019), -70 (0.059, 0.030), and -89 (slow exchange).

Discussion

To interpret the spectra and to define the conformational properties of the sulfimides, criteria must first be developed for determination of the imide configuration.[8] Criteria based on the magnitude of the chemical-shift difference between the α protons, $\delta_{ae}(\alpha)$, have been firmly established for the isoelectronic sulfoxides, first in thiane 1-oxide[4a] and later for many other examples,[9]

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[8] J. B. Lambert, C. E. Mixan, and D. S. Bailey, *Chem. Commun.*, 316 (1971).

[9] A. B. Foster, T. D. Inch, M. H. Qadir, and J. M. Webber, *ibid.*,

Table I. Spectral Parameters for Thiane Sulfimides, Sulfoxides, and Sulfoximides[a]

	3	5	6	7	8	9[b]
$\delta_{ae}(\alpha)$	49.8	*c*	33.2	30.8	74.8	78.3[d]
$\lvert J_{ae}\rvert(\alpha)$	12.0	*c*	12.0	12.4	13.7	11.7
Pop.	0.55	*c*	0.40	0.45	0.67	0.38
$\delta_{ae}'(\alpha)$	14.4	*c*	2.0	3.2	47.6	43.2[d]
$\lvert J_{ae}'\rvert(\alpha)$	13.8	*c*	14.4	14.7	14.8	13.7
Pop.′	0.45	*c*	0.60	0.55	0.33	0.62
$\delta_{ae}(\gamma)$	34.1	40.5[d,e]	40.0	40.0	40.2	30.6[d]
$\lvert J_{ae}\rvert(\gamma)$	14.0	14.1[e]	14.4	14.0	14.8	14.0
Pop.	0.45		0.60	0.55	0.33	
$\delta_{ae}'(\gamma)$	39.6	40.5[d,e]	41.6	41.4	45.2	36.2[d]
$\lvert J_{ae}'\rvert(\gamma)$	13.8	14.1[e]	14.2	14.0	14.4	14.3
Pop.′	0.55		0.40	0.45	0.67	
Solvent	CH_2Cl_2–$CHClF_2$	CH_2Cl_2	$CHClF_2$	$CHClF_2$	$CHClF_2$	CH_2Cl_2
Temp, °C	−85	−85	−89	−89	−89	−90
$\Delta G°$, kcal/mol[f]	+75	*c, e*	−145	−70	±250	−175

[a] All chemical-shift differences are in hertz at 90 MHz and the coupling constants are in hertz; δ, J, and pop. (population) refer to the lower field isomer; δ', J', and pop.′ refer to the higher field isomer. [b] Data from ref 4a. [c] The α resonance of **5** remains a broad singlet over the entire range of observation. [d] Data from 60 MHz converted to 90 MHz. [e] Only one γ AB quartet is observed for **5**; either both isomers have the same parameters or one is absent. [f] A positive sign of ΔG denotes an excess of equatorial imide.

Table II. Activation Parameters for Ring Reversal[a]

Compd[b]	E_a, kcal/mol	log A	$\Delta G_c^{\ddagger}$,[c] kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Corr coef
3	13.9	16.1	10.5 (−59)	13.3	13.1	0.999
5	14.1	16.7	10.2 (−65)	13.5	15.9	1.000
6	14.2	16.4	10.5 (−57)	13.6	14.3	0.995
8	12.6	15.0	10.3 (−58)	12.0	8.0	0.997
9[d]	14.2	17.1				

[a] These parameters are the mean of the values for the individual conformers, *e.g.*, **3a** and **3e**. [b] Solvent information is given in Table I. [c] Free energy of activation at the coalescence temperature, calculated from $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. [d] Data from ref 4a.

including the penicillin oxides.[10] Invariably, $\delta_{ae}(\alpha)$ is observed to be larger for the equatorial oxide isomer (axial lone pair) than for the axial oxide isomer. A consistent criterion for sulfoxide configuration has also been based on the magnitude of the geminal coupling constant between the α protons,[11] whereby $J_{ae}(\alpha)$ is larger (more negative) for the axial oxide isomer than for the equatorial oxide isomer.

Examination of Table I reveals that similar correlations exist for the sulfimides **3**, **6**, and **7**. In all three cases, the isomer with the larger chemical-shift difference has the smaller coupling constant and resonates at the lower field (the unprimed parameters in Table I). By analogy with the sulfoxides, these properties should be characteristic of the isomer with an equatorial imide group and an axial lone pair. The remaining (primed) data in Table I [smaller $\delta_{ae}'(\alpha)$, larger $J_{ae}'(\alpha)$, higher field center of resonance] must refer to the axial imide–equatorial lone pair isomer. The properties of the lone pair that give rise to these correlations have been discussed in connection with the sulfoxide configuration.[4a,9–11] It is noteworthy that the γ protons, which are not vicinal to a lone pair, give nearly identical values of $\delta_{ae}(\gamma)$ and $J_{ae}(\gamma)$ for both isomers. Isomer assignments for the γ protons were made by comparison of populations with those measured from the α protons, for which an assignment had been made.

Of the three configurational correlations, the most reliable is probably that derived from $J_{ae}(\alpha)$. Although the $\delta_{ae}(\alpha)$ correlation has not yet failed for sulfoxides,[9–11] we have found that it fails in one case for a sulfimide. In 4,4-dimethylthiane-1-(*N*-tosyl)imide, the equatorial imide isomer has the smaller value of $\delta_{ae}(\alpha)$. The geminal methyl groups, particularly the one at the axial position, have a strong effect on the chemical shifts of the α protons,[12] so an exception is not unexpected. In simple, unsubstituted cases, $\delta_{ae}(\alpha)$ is probably a useful configurational probe, but $J_{ae}(\alpha)$ appears to be reliable in all cases since it is less sensitive to distant substituents. For any particular assignment, both diastereomers should be on hand.

With three mutually consistent criteria for imide configuration, the isomer assignment should be quite reliable. The populations of the two conformations become the next point of interest. Thiane 1-oxide exists preferentially (62%, 175 cal/mol at −90°) in the form with an axial oxide.[4a] Similarly, both of the *N*-sulfonyl compounds (**6** and **7**) exhibit an axial preference, though to a somewhat lesser extent (145 cal/mol in **6** and 70 in **7**). The axial preference of the oxide has been attributed to attractive interactions between the axial oxygen atom and other nuclei in the molecule, particularly the 3,5-axial protons.[13] A similar explanation may hold for the sulfonylimides. Certainly, the sulfonyl group must be directed away from the center of the ring, as in

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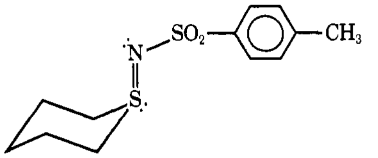
the drawing below of *anti*-**6a**. The steric interactions of the bulky tosylimide group become unimportant, and the conformational preference is determined primarily by the interactions of the nitrogen atom and its lone pair with the atoms in the rest of the molecule.

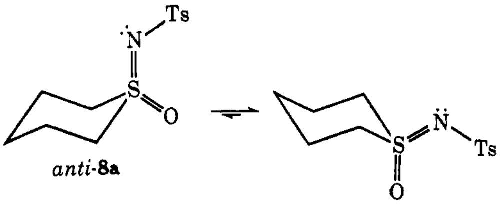


6a

In none of the spectra were the α protons from one side of the ring observed to be magnetically nonequivalent to those on the other side. Therefore, either S–N rotation is fast on the nmr time scale, or the N substituent lies on the plane determined by the nitrogen atom, the ring sulfur atom, and C-4 of the ring.

Contrary to all other examples, the substituent on sulfur in the parent thian-1-imide (**3**) exhibits a small preference (75 cal/mol) for the equatorial position. This preference may arise from greater ease of intermolecular hydrogen bonding of the NH group in the equatorial isomer. All the values of $\Delta G°$ are quite small (Table I), so a definitive interpretation of the differences is difficult. Conformational effects are quite evenly balanced in these molecules, so that a small factor might tip the equilibrium in one direction or the other.

The above configurational criteria do not apply to the sulfoximides **5** and **8**. In **5**, no equilibrium data could be obtained from the spectra because of the accidental coincidences present in both the α and γ resonances. For **8**, however, resonances from two isomers (eq 4)



(4)

anti-**8a**

anti-**8e**

in the ratio 2:1 could be readily discerned. Although we have no guaranteed method for an assignment, the more populous isomer is probably **8e**, with an equatorial imide and an axial oxide. We base this judgment on the fact that all the imides (**3**, **6**, and **7**) show a smaller preference for the axial position than does the oxide **9**.[14]

The barriers to ring reversal in **3**, **5**, **6**, **8**, and **9** are quite similar (Table II) but consistently larger by about 3 kcal/mol than those measured for cyclohexane, thiane, or tetrahydropyran.[4,8] Because the range of free-energy differences is much smaller, the variance in $\Delta H^{\neq}$ may be due to the inaccuracy of $\Delta S^{\neq}$ as determined by the nmr method.

By way of summary, we have observed two conformational isomers at equilibrium in the low-temperature nmr spectra of the 1-imide, the 1-(*N*-tosyl)imide, the 1-(*N*-benzenesulfonyl)imide, and the 1-(*N*-tosyl)imide 1-oxide of thiane. Barriers to ring reversal were obtained by the complete line-shape method. For the sulfimides, the equatorial isomer could be identified by a larger $\delta_{ae}(\alpha)$, a smaller $J_{ae}(\alpha)$, and a lower field center point of the AB spectrum. These criteria may be general for sulfimides. For the *N*-sulfonylimides (**6** and **7**), the more highly populated isomer has the imide group axial, whereas in the parent thian-1-imide (**3**), the preference is for an equatorial imide group.

Experimental Section

Infrared spectra were measured on a Beckman IR-5. Routine nmr spectra were recorded on Varian A-60 and T-60 spectrometers. Low-temperature experiments were carried out on the Bruker HFX-10 at 90 MHz.[15] Computer analyses were performed on a CDC-6400 with Calcomp plotting accessories. Elemental analyses were performed by Miss H. Beck, Analytical Services Laboratories, Department of Chemistry, Northwestern University, and Micro-Tech Laboratories, Inc., Skokie, Ill.

Thiane-*3,3,5,5-d*$_4$ was prepared by a method described elsewhere.[4]

Thiane-1-(*N*-tosyl)imide (6).[16] In a 125-ml, round-bottomed flask, 1.0 g (0.01 mol) of thiane and 3.8 g (0.02 mol) of chloramine-T (Matheson Coleman and Bell) were mixed in distilled H_2O and stirred for 30 min. The clear solution became cloudy, and a white precipitate developed. The mixture was extracted with three 25-ml portions of $CHCl_3$. Evaporation of the $CHCl_3$ left a viscous yellow oil, which solidified after a washing with anhydrous ether. The solid was recrystallized from benzene and dried to give 2.25 g (83%) of **6**, white crystals, mp 148–149°. *Anal.* Calcd for $C_{12}H_{17}NO_2S_2$: C, 53.10; H, 6.27; N, 5.10. Found: C, 53.04; H, 6.31; N, 5.19.

Thiane-1-(*N*-benzenesulfonyl)imide (7)[16] was prepared in the same manner as **6** from 1.75 g of chloramine-B (K & K Laboratories) and 0.5 g of thiane. The yield was 1.05 g (82%), mp 133°. *Anal.* Calcd for $C_{11}H_{15}NO_2S_2$: C, 51.36; H, 5.84; N, 5.45. Found: C, 51.48; H, 6.13; N, 5.33.

Thian-1-imide (3).[6] To a stirred solution of 3 g of thiane and 0.72 g of sodium in absolute methanol was added a solution of 4.2 g of hydroxylamine-*O*-sulfonic acid (Alfa Inorganics) in absolute methanol previously prepared at −30°. A white precipitate developed immediately. The reaction was stirred at room temperature overnight. The solid was isolated by filtration, and the filtrate was concentrated at reduced pressure until additional solid appeared. Anhydrous ether was added to precipitate more solid, which was isolated by filtration. The filtrate was concentrated further to give a small amount of yellow oil, which eventually solidified in a vacuum desiccator over P_2O_5. The total yield of solid (the sulfimidium salt) was extracted with liquid ammonia in a Soxhlet-like apparatus. The ammonia extract was evaporated to give 1.35 g (40% from thiane) of a yellow liquid, which decomposes to thiane above −10°.

Conversion of 3 to 9. To a solution of 0.42 g of thian-1-imide (**3**) in 3 ml of H_2O was added 0.15 g of NaOH in 3 ml of H_2O. The mixture was stirred for 1 hr and neutralized with dilute H_2SO_4. The solution was extracted with CH_2Cl_2, and the organic material was dried over $MgSO_4$. Evaporation of the solvent produced thiane 1-oxide (**9**), which was spectrally identical with authentic material.[4a]

Conversion of 3 to 5. To a solution of 0.70 g of thian-1-imide in 5 ml of H_2O was added 0.6 g of $KMnO_4$ in 20 ml of H_2O. The reaction was stirred at 40° until all the $KMnO_4$ had been consumed. The mixture was filtered to remove the inorganics and extracted with $CHCl_3$. The organics were dried ($MgSO_4$) and concentrated to give a colorless oil, which under vacuum produced 0.23 g of thian-1-imide 1-oxide (**5**), spectrally identical with the authentic material.

Thian-1-imide 1-Oxide (5). To 0.82 g of thiane 1-oxide (**9**)[4a] in 25 ml of $CHCl_3$ were added 1.9 g of solid sodium azide and 1.9 ml of concentrated H_2SO_4. The reaction mixture was heated at 50–55° for 60 hr. The mixture was cooled, H_2O was added, and the $CHCl_3$ layer was removed. The aqueous layer was extracted three times with $CHCl_3$, and the organic portions were combined and dried ($MgSO_4$). The solvent was removed; the residual oil solidified under vacuum to give back unreacted sulfoxide. The aqueous portion was made slightly basic with 10% NaOH solution and extracted several times with $CHCl_3$. The organic extract was dried

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(14) Experiments with the 3,3-dimethyl derivatives of **6** and **9** confirm this assignment.

(15) We thank the National Science Foundation for an equipment grant to purchase signal-averaging accessories for the HFX-10.

(16) F. G. Mann and W. J. Pope, *J. Chem. Soc.*, **121**, 1052 (1922).

over $MgSO_4$ and concentrated. The remaining oil produced under vacuum solid sulfoximide, 0.43 g (46%), which was recrystallized from ethyl acetate at −78° to give 0.26 g of the hygroscopic sulfoximide **5**.

Thiane-1-(*N*-tosyl)imide 1-Oxide (8). Tosyl chloride (2.15 g) and thian-1-imide 1-oxide (**5**, 0.75 g) were stirred in 30 ml of dry pyridine at room temperature for 24 hr. Water was added, and the mixture was extracted with $CHCl_3$. Evaporation of the $CHCl_3$ produced a yellow liquid, to which toluene was added in order to remove the pyridine as an azeotrope. The volume was reduced in this manner to about 5 ml. Concentration under reduced pressure left a white solid, which was recrystallized from ethyl acetate to give 1.2 g (75%) of white crystals, mp 136–137°. *Anal.* Calcd for $C_{12}H_{17}NO_3S_2$: C, 50.17; H, 5.92; N, 4.87. Found: C, 50.04; H, 6.00; N, 4.87.

Tracer Studies of Acid-Catalyzed Reactions. XI. Stereoselectivity in Alcohol Dehydration over Hydroxyapatite and Alumina Catalysts

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Abstract: The reactions of model compounds (*threo-* and *erythro*-2-butanol-*3-d*$_1$ and *cis-* and *trans*-2-methylcyclohexanol) were used to characterize the surfaces of alumina and calcium-deficient hydroxyapatite catalysts. Over alumina, the butenes formed by dehydration contained the following percentages of the monodeuterated molecules: 94% of the 1-butene, 80% of the *trans*-2-butene, and 28% of the *cis*-2-butene from the threo stereoisomer and 94, 28, and 84%, respectively, from the erythro compound. Over hydroxyapatite, the corresponding results were 95, 29, and 74% for the threo, and 95, 80, and 39% for the erythro stereoisomer. Thus, anti elimination was the preferred mode over alumina and syn elimination over hydroxyapatite. The results from the cyclohexanols were not so straightforward. Anti elimination by both catalysts was indicated for *cis*-2-methylcyclohexanol. The ratio of 1-methylcyclohexene to 3-methylcyclohexene found for hydroxyapatite (3.0) was in good agreement with that reported by Pines and Blanc for alumina. With the trans isomer, however, the ratio for hydroxyapatite (1.1) was much higher than that reported for alumina (0.14–0.37). With both catalysts, the cis isomer reacted a little faster than the trans, and 25–35% of the deuterium from *trans*-2-methylcyclohexanol-*2-d*$_1$ was retained in the 1-methylcyclohexene product. Over hydroxyapatite, the kinetics were zero order in reactant and activation energies were about 26 and 30 kcal/mol, respectively, for methylcyclohexanol and 2-butanol. Saytzeff elimination was favored over Hofmann with both catalysts.

Several studies of the stereospecificity of alcohol dehydration to olefins over metal oxide catalysts have been made.[2-4] Pines and coworkers found that the olefin product distributions in dehydration of primary and secondary alcohols over alumina approached those expected for a concerted anti elimination.[2,3] It was proposed that dehydration takes place in pores or crevices in the alumina surface, with the alcohol molecules situated between an acidic site on one surface and a basic site on another. Lundeen and Van Hoozer,[4] however, showed that dehydration of secondary alcohols over a thoria catalyst occurred mainly *via* syn elimination, and that Hofmann elimination was strongly favored over Saytzeff. They suggested that these results stemmed from stringent steric requirements which they envisioned for formation of the transition state with their system, but noted that strong carbanion character in the transition state would favor Hofmann elimination.

Dehydrations of primary and secondary alcohols over hydroxyapatite (basic calcium phosphate) catalysts yielded olefin product distributions which were similar to those obtained in dehydrations of the corresponding alcohols over alumina,[5] except that the cis/trans ratios tended to be lower. The hydroxyapatite used was not porous; its surface area was made up almost entirely by crystal faces.[6] Consequently, there was very little possibility of anti elimination in crevices as proposed for alumina. Moreover, the low selectivity for 1-alkene formation from secondary 2-alkanols over hydroxyapatite suggested that should syn elimination be found, the reaction could not be comparable with that on thoria.

The present paper concerns an attempt to use the reactions of model alcohols to describe properties of the catalyst surface, *e.g.*, the nature of the catalytic sites and of the transition state. It was hoped that the rapidly growing knowledge of these matters in homogeneous media could be translated to this end. The reader should recognize, therefore, that it was not our purpose to debate the controversial mechanistic points. Data are presented confirming that anti elimination predominates over alumina and showing that syn elimination is favored with 2-butanol over hydroxyapatite. Complete stereospecificity was not achieved, however, over either catalyst.

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