Syn–Anti Isomerism in an *N*-Benzenesulfonylimine. The Mechanism of Stereomutation at the Carbon–Nitrogen Double Bond[1,2]

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Abstract: Chemical-shift nonequivalence in the room-temperature spectrum of *N*-(1,2,3-trimethyl-2-butenylidene)-benzenesulfonamide (**1**) indicates the presence of two isomers in solution resulting from syn–anti isomerism. Using nuclear magnetic resonance spectroscopy the ratio of the isomers in solution at room temperature was determined to be 1.7, with the low-field isomer predominating. However, crystallization of **1** yields the minor upfield isomer exclusively. Equilibrium studies indicate that entropy, rather than enthalpy, is the predominant factor determining the stabilities of the two isomers at temperatures above 150°K. The activation parameters for stereomutation of **1** have been determined using complete line-shape analysis (CLS) and by a combination of rates determined by CLS with rates determined by equilibration at low temperatures. The comparison of Arrhenius data obtained using both procedures indicates that the exclusive use of CLS may prove to be unreliable but that when used in conjunction with another method, accurate results can be obtained. In addition, the free energy of activation at the coalescence temperature obtained from CLS was compared with that calculated using the approximate equation $k = \pi\Delta\nu/\sqrt{2}$. The two were found to be essentially the same. The mechanisms that have been proposed for syn–anti isomerism in imines, nitrogen inversion, torsion about the carbon–nitrogen double bond, and a mechanism intermediate between these two extremes, have been critically discussed. The *N*-benzenesulfonyl group has been found to be more effective at lowering the barrier to syn–anti isomerism than an *N*-phenyl substituent. This result indicates that the mechanism of isomerization cannot be pure inversion, but that the mechanism has some torsional character.

The stereochemical properties of the carbon–nitrogen double bond have been the subject of numerous investigations in recent years.[3–10] Of particular concern has been the question of the mechanism of stereomutation in these compounds. In some respects, this controversy has paralleled that concerning the mechanism of conformational interchange in acyclic trisubstituted nitrogen compounds which bear heteroatoms bonded to nitrogen. The identity of the slow conformational change in such compounds including aminophosphines, hydroxylamines, hydrazines, and sulfenamides as inversion at nitrogen or torsion about the nitrogen–heteroatom bond has been a topic of lively debate.[11–15] Likewise, opposing views identifying the mechanism of syn–anti isomerism in imines as either inversion or torsion have been presented and supported by experiment.

The mechanism which has been supported by most workers has been the inversion or lateral-shift mechanism.[3–7] Five main arguments have been adduced in support of this mechanism. In the first place, the relatively low barriers in imines as compared with olefins have been used to suggest that the mechanisms for these two cis–trans isomerizations must be fundamentally different.[3] The similarity in the effect of substituents in para-substituted anilides to that in corresponding aziridines has been used to argue that the mechanisms of stereomutation must be similar.[4] On the other hand, the difference in steric effects between the barriers in imines and those in the corresponding immonium salts (which must isomerize by rotation) has been used to support the proposition that the two systems isomerize by different mechanisms.[4] Fourth, the effect of solvent on the barrier (an increase in hydrogen bonding solvents) has been adduced in favor of an inversion mechanism.[4] Finally, Kessler has investigated interrelated processes involving both syn–anti isomerization at an imine double bond and slow rotation about the imino *N*-aryl single bond in substituted anils.[4e] It was argued that the relationship between the two processes must depend on whether syn–anti isomerization occurred *via* a torsional or inversional pathway. The relationship found was alleged to provide evidence that torsion about the imine double bond must be slow compared with syn–anti isomerism.

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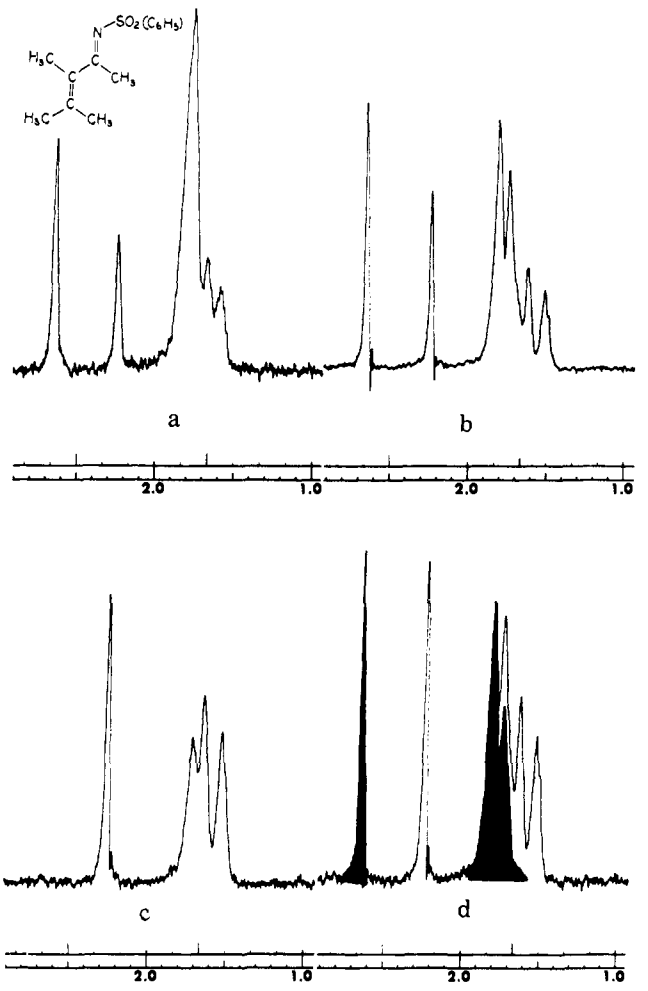


Figure 1. Nmr sepctra of **1** in methylene chloride: (a) room temperature; (b) dissolved at room temperature, spectrum measured at −57°; (c) dissolved at −70°, spectrum measured at −57°; (d) spectrum c subtracted from a spectrum of a 1:1 mixture of the two isomers measured at −57°. The shaded portion of the spectrum is the resultant.

The most convincing experimental evidence in favor of the torsion mechanism is the effect of heteroatoms with lone pairs of electrons which dramatically lower the isomerization barrier when attached to the imino carbon atom[8] although the effect of substituents at the nitrogen atom can also be rationalized using the torsion model.[9] The similarity in the barriers in imines and their corresponding *N*-oxides (nitrones) has also been used to favor the torsion model.[10]

We describe in this paper the results of our experimental investigation of syn–anti isomerism in an *N*-benzenesulfonylimine and its relevance to the mechanism of stereomutation of imines, in general.

Results

Although there are several reports in the literature of syn–anti isomerism in *N*-arenesulfonylimines,[4,7,16] quantitative data concerning the effect of the arenesulfonyl substituent on the barrier to isomerization in a simple ketimine were sparce. A knowledge of this effect can provide information which is pertinent to the evaluation of the relative merits of the two alternate

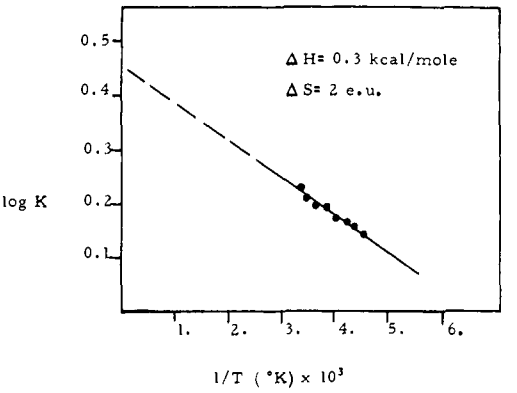
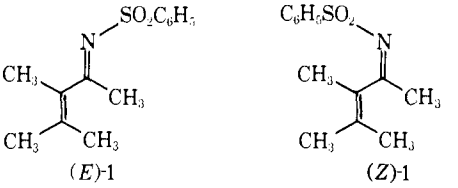


Figure 2. Plot of log equilibrium constant *vs.* the reciprocal of the absolute temperature.

mechanisms for isomerization in correctly predicting the effect of substitution at nitrogen. *N*-(1,2,3-Trimethyl-2-butenylidine)benzenesulfonamide (**1**) represented a useful compound for this study. Chemical-shift nonequivalence in the room-temperature nmr spectrum had been reported although this was not originally attributed to syn–anti isomerization at the carbon–nitrogen double bond.[17] At room temperature, **1** exhibits two singlets for the methyl group attached to the imino carbon atom reflecting the presence of two isomers in solution (Figure 1a). The ratio of signals indicates an equilibrium constant of 1.7 favoring the isomer which resonates at lower field.

Surprisingly, the preference for the low-field isomer apparently derives from the difference in the entropies of the two isomers rather than from the difference in enthalpies. This can be seen qualitatively, by comparing the room-temperature spectrum with that taken at −50° in which the equilibrium constant is substantially lower (Figure 1b). A plot of the logarithm of the equilibrium constant against the reciprocal of the temperature in degrees Kelvin (Figure 2) furnished thermodynamic parameters: $\Delta H = +0.3$ kcal/mol, $\Delta S = +2$ eu, $\Delta G_{300°} = -0.3$ kcal/mol. Thus, the low-field isomer predominates in the equilibrium at temperatures above *ca.* 150°K, the isergonic temperature at which the two isomers have the same free energy of formation. Below this temperature the population of the upfield isomer should predominate since it has the more negative enthalpy of formation.

It is noteworthy that crystals of **1** are isomerically homogeneous. Since the two isomers of **1** are in equi-



librium, crystallization of one of them displaces the equilibrium so that the more easily crystallized isomer may be isolated. This phenomenon is analogous to that observed when optically active diastereomers which are configurationally labile at one asymmetric center are allowed to crystallize, often resulting in

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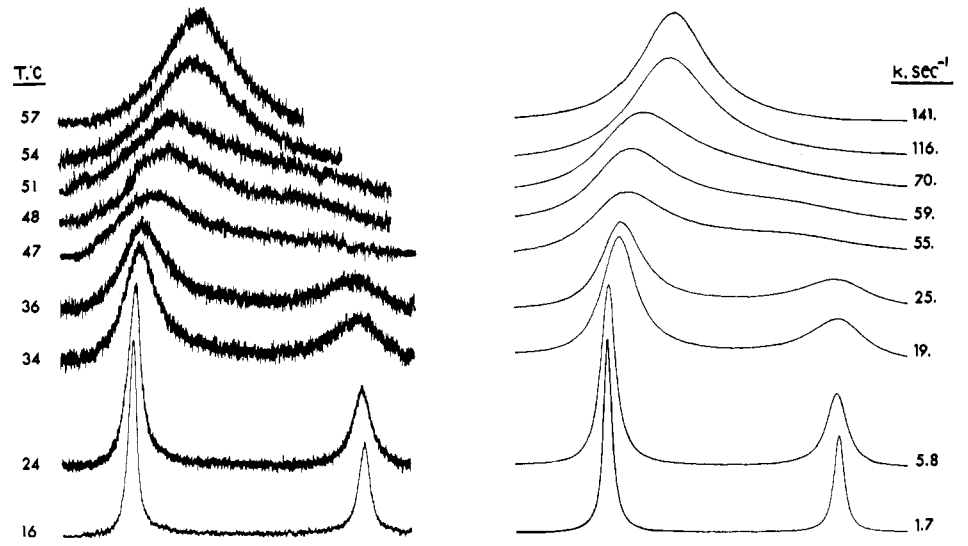

Figure 3. Comparison of theoretical and experimental nmr spectra for **1**.

partial or complete resolution at the labile center. This has been termed equilibrium asymmetric transformation.[18] While the history of this term has for the most part involved optically active compounds, the presence of optical activity or even asymmetry is not crucial to the occurrence of this phenomenon. Rather, a mobile equilibrium between diastereomers is required, which can be displaced by the crystallization of one of them. In the present instance, we prefer to term the phenomenon diastereomeric transformation, since both isomers are achiral.

At temperatures below $-70°$ isomerization is slow, and dissolution of crystalline **1** results in a solution containing only the isomer which resonates at higher field and which possesses the more negative enthalpy of formation. In the crystalline form degrees of freedom corresponding to bond stretching, angle deformation, and bond torsion are removed and it is possible that the minor isomer crystallizes preferentially since it is lower in enthalpy and hence in the crystalline form it will be lower in free energy as well. Of course, it is also possible that different crystal-packing forces for the two isomers are large enough to outweigh any small difference in enthalpies.

A definitive assignment of configurations to the two isomers is not possible on the basis of available information. Examination of models of the two isomers indicates that the *E* isomer[19] is more flexible than the more congested *Z* isomer.[19] On the basis of the entropy difference it would be appealing to assign the *E* configuration to the downfield isomer. This assignment would be in accord with the suggestion that the chemical-shift difference between the α-methyl group in the two isomers is due to long-range deshielding by the sulfonyl group in the *E* isomer.[16,17] However, on this basis, one might expect the β-methyl group in *Z*-**1** to resonate at lower field as well. The spectrum of one isomer can be obtained directly as described above (Figure 1c). The spectrum of the other isomer can be obtained by subtraction of spectrum 1c from the spectrum of an equal mixture of the two isomers (Figure 1d). Comparison of the two indicates that all of the methyl groups in one isomer resonate at lower field than those in the other isomer. It is possible that in the *Z* isomer steric hindrance prevents a coplanar relationship between the olefin and imino double bonds and that the proper geometry for deshielding does not obtain. A more serious objection to this assignment is the necessity of assigning the *Z* configuration to the isomer with the lower enthalpy. It is difficult to see why *Z*-**1** should have a lower enthalpy than *E*-**1** in which steric hindrance is reduced and conjugation between the olefin and imino double bonds should be greater.

Having isolated the minor isomer in solution by diastereomeric transformation, we were able to measure the rate of syn–anti isomerization using two different, independent methods. Upon raising the temperature to temperatures between -60 and $-50°$, relaxation to an equilibrium mixture of isomers occurred at a rate measurable on the isolation time scale. The rate of equilibration was measured at -57, -54, and $-52°$. Below $-57°$ solubility problems prevented convenient measurement while above $-52°$ the rate was fast enough that a sufficient number of spectra could not be recorded before equilibrium was reached.

The rate of interconversion could also be determined by investigating the collapse of the two singlets into a single resonance as the rate of interconversion becomes fast on the nmr time scale. A computer program based on the solution to the Bloch equation with exchange terms was used to calculate and plot theoretical spectra corresponding to various rates of exchange. These were matched to experimental spectra using a combination of extrapolation, and trial and error (Figure 3).

An approximate equation has been widely used to obtain the rate at the coalescence temperature, the temperature at which the minimum between the two peaks just disappears. This equation is not strictly valid if the populations of the two exchanging sites are not equal or if the lines are broadened by spin–lattice relaxation or magnet inhomogeneity. Since rates and free

$$k_c = \pi\Delta\nu/\sqrt{2}$$

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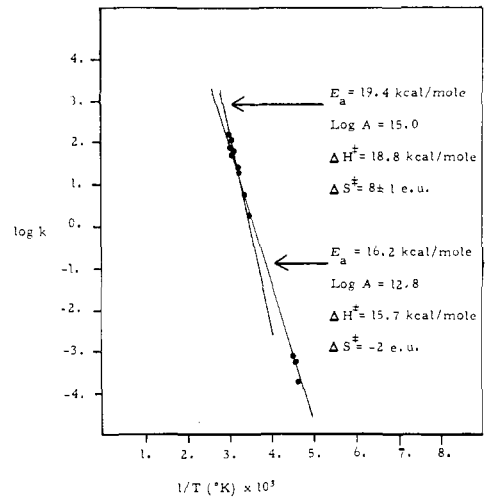

Figure 4. Arrhenius plots of log rate constant *vs.* reciprocal absolute temperature for **1**: (a) obtained from complete line-shape analysis only; (b) obtained from both equilibration and complete line-shape analysis.

energies obtained using this equation have been criticized as unreliable, we wish to point out that in this case the free energies of activation obtained using complete line-shape analysis and the approximate equation were virtually the same: complete line-shape analysis, k_c = 70 sec^{-1}, $\Delta G^{\ddagger}$ = 16.3 kcal/mol; approximate equation, k_c = 56 sec^{-1}, $\Delta G^{\ddagger}$ = 16.4 kcal/mol. We have previously found that free energies of activation for nitrogen inversion in an isoxazolidine calculated using the approximate equation also are in good agreement with the results of complete line-shape analysis.[20] The reliability of this approximate equation for the uncoupled AB spin system with an equilibrium constant of 1–3 now seems to be general.

Two separate Arrhenius plots were constructed using the rates obtained (Figure 4). The first analysis used only the points derived from complete line-shape analysis and furnished the following activation parameters: E_a = 19.4 ± 0.8 kcal/mol, log A = 15.0 ± 0.6 sec^{-1}, $\Delta H^{\ddagger}$ = 18.8 ± 0.8 kcal/mol, $\Delta S^{\ddagger}$ = 8 ± 3 eu. The correlation coefficient was 0.993. The substantial entropy of activation is at variance with that expected for an isomerization which involves neither bond making or bond breaking at the transition state nor substantial changes in nonbonded interactions. The rates obtained in both temperature ranges used in a second Arrhenius analysis afforded the following parameters: E_a = 16.2 ± 0.3 kcal/mol, log A = 12.8 ± 0.2 sec^{-1}, $\Delta H^{\ddagger}$ = 15.7 ± 0.3 kcal/mol, $\Delta S^{\ddagger}$ = −2 ± 1 eu. Since the temperature range over which rates could be measured is over 100°, the reliability of the entropy of activation obtained is greater than that obtained using line-shape analysis alone. As expected, we find that the entropy of activation is quite small. This is in contrast to numerous complete line-shape analyses of compounds undergoing conformational interchange, including that described for **1**, in which substantial positive and negative entropies of activation have been obtained. We concur with the view that the combination of line-shape and direct kinetic measurements is the method of choice for obtaining activation parameters and that complete line-shape analyses of compounds undergoing conformational interchange which furnish large positive or negative activation entropies must be treated with suspicion unless the temperature range is at least *ca.* 100°.

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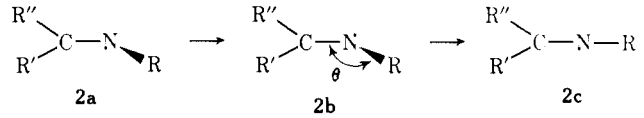
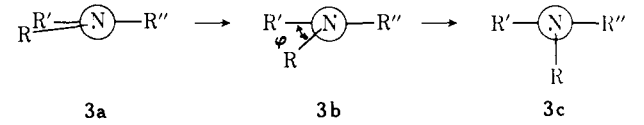
Discussion

Three mechanisms have been proposed for isomerization in imines: (a) inversion at divalent nitrogen or "lateral shift," (b) torsion about the imino double bond, and (c) a mechanism intermediate between these two extremes. The progress of the lateral-shift mechanism along the reaction coordinate is described by a progressive increase in θ, the CNR angle, from *ca.* 120 to 180° at the transition state (**2a** → **2c**). The activation energy

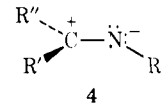


is associated with the propensity of the imino nitrogen to achieve a geometry corresponding, approximately, to sp^2 hybridization. It represents the energy needed to effect a progressive diminution in the p character of the nitrogen atomic orbital used in the C–N σ bond and a progressive increase in the p character of the lone-pair orbital until the sp hybridization of the transition state is reached.

The torsional mechanism can likewise be described as a gradual change in a single parameter, φ, the R′CNR dihedral angle (**3a** → **3c**). The angle φ is increased



from zero in the ground state until it is 90° at the midway point along the reaction coordinate. The increase in energy along the reaction coordinate is occasioned by the decreased overlap between the carbon p orbital and the orbitals on nitrogen. Since the nitrogen atom is considerably more electronegative than carbon, the transition state is usually written as a dipolar species **4**, indicating a substantial contribution of



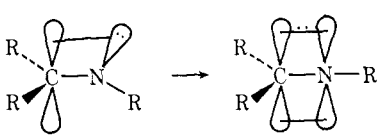
the canonical form possessing a formal negative charge on nitrogen. However, even in the φ = 90° conformation there must be some overlap between the nitrogen lone pair orbital and the imino carbon p orbital which will diminish the charge separation. In fact, semiempirical MO calculations indicate substantial π bonding at the torsional transition state.[1] Although the bond order of the imino C–N bond is diminished upon torsion some multiple bonding remains even at the transition state.

Unlike the situation in such conformational interchanges as the degenerate racemization, or topimerization,[4d] of sulfenamides, hydroxylamines, and hydrazines, where both processes are required, either torsion or inversion alone can effect syn–anti isomerization in imines. This alternative duality of mechanism can be

expressed by a two-dimensional reaction coordinate (Figure 5). The upper right and lower left corners represent the ground states of the two syn and anti isomers (or the ground states of two topimers[4d] when the two substituents attached to the imino carbon atom are the same). The upper left corner represents the inversional transition state ($\theta = 180°$) and the lines connecting this point to those representing the ground states represent a folded reaction coordinate expressed in θ. Similarly, the lower right corner point corresponds to the torsional transition state ($\varphi = 90°$) and the lower and right edges comprise a folded torsional reaction coordinate expressed in φ. When the imino carbon substituents are identical (R′ = R″), the diagonal connecting the inversion and torsion transition states is an element of two-dimensional mirror symmetry (mirror line) dividing the forward and reverse approaches to the transition state. The points along the mirror line represent structures wherein $\varphi = 90°$ and θ varies from 120 to 180°.

The two termini of the mirror line are not the exclusive possibilities for the isomerization transition state, but the points on the mirror line represent a continuum of possible transition states which stretch from pure inversion (upper left terminus) to pure torsion (lower right terminus). The infinitude of lines or curves connecting the nonterminal points of the mirror line with the ground states represent a series of mechanisms intermediate between pure inversion and pure torsion.

Two lines of reasoning suggest that the isomerization may proceed *via* a transition state corresponding to one of the nonterminal points on the mirror line. First, we note that a torsional barrier is undefined at the inversional transition state. For geometries with values of θ arbitrarily close to 180°, the torsional barrier must be arbitrarily small ($\lim_{\theta \to 180°} \Delta G^*_{\text{torsion}} = 0$). Inversion along the left coordinate (corresponding to $\varphi = 0°$) does not result in a substantial change in the C–N bond order. By contrast near the torsion terminus an increase in θ is accompanied by an increase in the p character of the nitrogen lone pair orbital which is geometrically situated so as to be able to overlap with the carbon p orbital, thus increasing the C–N bond order (**5a** → **5b**). Because of this additional stabilization



5a **5b**

with increased θ the inversion barrier must reach a minimum as the torsional transition state is approached.

As a complementary view to this one, we may focus upon the structural reasons for the increased energy at the transition state. Increasing θ leads to increased energy because of the relative instability of sp hybridization at nitrogen while increasing φ leads to decreased C–N multiple bonding. We can limit the destabilization due to either factor by moving the transition state along the mirror line. However, decreasing the destabilization of one factor is accompanied by increased destabilization due to the other factor. For example, moving downward and to the right along the mirror line diminishes the energy increase due to unfavorable

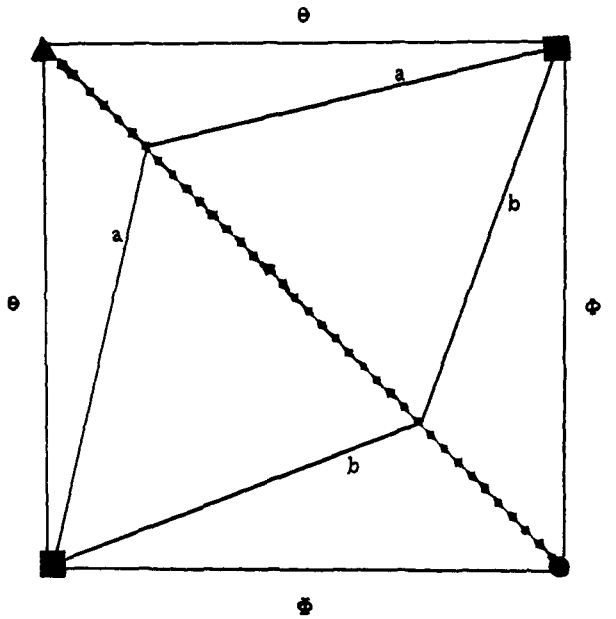


Figure 5. Intermediate mechanism diagram: ■ represents the topimeric or syn and anti isomeric ground states; ▲ represents the pure inversion transition state; ● represents a pure torsion transition state; ◆◆ represents the mirror line; a represents a reaction coordinate for an intermediate, but predominantly inversional mechanism; b represents a reaction coordinate for an intermediate but predominantly torsional mechanism.

hybridization but concomitantly decreases the C–N bond order. The position of the transition state, the minimum energy along the mirror line, is determined by the balance between two factors and it seems likely that the position can be shifted by structural and medium variations. Substituents which diminish the importance of C–N multiple bonding in the ground state should have the effect of shifting the transition state toward the torsion terminus while substituents which facilitate the rehybridization at nitrogen should shift the transition state toward the inversion terminus.

It is possible to account for all of the observed experimental facts in terms of a mechanistic continuum. Thus, the effects of different substituents at the imino nitrogen atom which have been observed are equally compatible with a transition state near the inversion terminus as well as pure inversion mechanism.

Semiempirical SCF–MO calculations[1] indicate that heteroatoms (O or N) bonded to the imino carbon atom lower the barrier to torsion about the CN double bond but raise the barrier to nitrogen inversion. Consequently, the lowering of syn–anti isomerization by such substituents[8] points to a torsional contribution to the mechanism and is incompatible with pure inversion. However, these substituent effects at the imino carbon atom can be accommodated by an intermediate mechanism as well as pure torsion. It is only necessary that the imino carbon become more positively charged in the transition state.

A similar situation applies to the solvent effects on the barrier and the comparisons with the analogs which bear an additional ligand at nitrogen. Although a strong dependence of the torsional barrier on solvent dielectric constant might be expected on the basis of a complete charge separation of the transition state, SCF–MO calculations[1] indicate that the torsion transition

state is not as polar as heretofore believed. Thus, the absence of a dependence on solvent dielectric constant[4] is not necessarily incompatible with a torsional contribution. The effect of hydrogen bonding solvents[4] (an increase in the barrier) points to substantial inversional character at the transition state but does not rule out the possibility of some torsional character to the transition state.

The effect of steric bulk on topimerization barriers in substituted anils[4] serves to place the transition state in the inversion region of the mirror line but again allows for the possibility of a torsional contribution. In any event the inclusion of this additional factor is expected to shift the transition state along the mirror line toward the inversion terminus. The absence of chemical-shift nonequivalence at temperatures above coalescence for syn–anti isomerization in an *N*-(2,4,6-triisopropylphenyl)guanidine has been adduced as evidence for the inversion mechanism.[4e] This experiment indicates that the transition state for syn–anti isomerization must be one in which the isopropyl methyl groups are enantiotopic. This can be accomplished only if the nodal plane of the aromatic ring is not coplanar with the guanidine moiety. While steric hindrance may prevent this orientation in a pure torsional transition state, models indicate that this geometry is accessible in an intermediate transition state.

This approach to the mechanistic possibilities in the imine system provides a framework for examining the effect of an *N*-arenesulfonyl group on the isomerization barrier. This effect can be assessed by comparison with an analogous *N*-phenyl ketimine. A convenient model for this purpose is *N*-isopropylidineaniline (acetone anil) whose barrier has been reported (T_c = 126°, $\Delta G_c^{\ddagger}$ = 20.3 kcal/mol).[7a] Since conjugation of the imino double bond with a phenyl group does not affect the barrier substantially we may expect the presence of the double bond in **1** to have a similarly minor effect. The difference between the barriers of acetone anil and of benzophenone anil ($\Delta G_c^{\ddagger}$ = 18.1 kcal/mol)[21] is only 2.2 kcal/mol. A single *C*-phenyl group, then, lowers the barrier by only about 1 kcal/mol and we would not expect a double bond to be of much greater consequence. On this basis, the arenesulfonyl group lowers the barrier by about 3 kcal/mol more than does a phenyl ring. A similar comparison may be made for barriers to stereomutation at the CN double bond in the quinone imine system using published data. Thus, the barrier in *N*-benzenesulfonyl-2,6-di-*tert*-butylquinoneimine, T_c = 44°, $\Delta G^{\ddagger}$ = 17.1 kcal/mol,[22] is considerably lower than in the corresponding *N*-phenyl analog, T_c = 140°, $\Delta G^{\ddagger}$ = 22.0 kcal/mol.[23]

This order of barriers is consistent with the dipolar torsion mechanism but not the inversion mechanism. The arenesulfonyl group is more effective at stabilizing a negative charge than is a phenyl ring; anilines are certainly less acidic than arenesulfonamides. Hence, this order is in accord with the dipolar mechanism. The expected order of free energies of activation for inversion follows from a comparison of the barriers in the appropriate aziridines in which only inversion is possible. The inversion barriers for *N*-phenylaziridine and *N*-benzenesulfonylaziridine are T_c = −40°, $\Delta G_c^{\ddagger}$ = 11.7 kcal/mol and T_c = −30°, $\Delta G_c^{\ddagger}$ = 12.4 kcal/mol,[24] respectively. This order is the reverse of that which obtains for the imines. The effect of the arenesulfonyl group, then, is added to other experimental evidence supporting a mechanism with some torsional character.

Experimental Section

N-(1,2,3-Trimethyl-2-butenylidene)benzenesulfonamide (**1**) was prepared as previously reported.[17] Recrystallization from petroleum ether gave crystals with mp 71–72° (lit.[17] 72–73°).

The nmr spectra were measured on a Varian A-60A spectrometer equipped with a Varian variable temperature probe using *ca.* 10% solutions. Temperatures were determined using methanol or ethylene glycol spectra as described in the Varian Manual. The coalescence point (used in the approximate expression for k_c) was assigned to the lowest temperature at which the minimum between the two resonances became a saddle point.

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 equation (program CLASS). The determination of rates of exchange by total line-shape analysis involved obtaining complete correspondence between experimental and theoretical spectra.

Equilibrium Measurements. Equilibrium constants were obtained by integration of the peaks in the nmr spectra of **1** in methylene chloride at various temperatures. In most cases three or more determinations were made at each temperature and averaged (Table I). A linear least-squares fit of the logarithm of the equilibrium constant as a function of the reciprocal of the absolute temperature gave: ΔH = 0.32 ± 0.02 kcal/mol and ΔS = 2.1 ± 0.1 eu. The error ranges refer to standard deviations. The correlation coefficient was 0.984. The difference in the free energies of the two isomers at the isergonic point and at room temperature are: ΔG_{150} = 0.0 kcal/mol and ΔG_{298} = 0.3 kcal/mol.

Table I

T, °C	*K*
24	0.59
13	0.62
−4	0.63
−15	0.64
−25	0.68
−38	0.69
−44	0.70
−53	0.71

Kinetic Measurements. The rates (Table II) used in preparing the Arrhenius plots were determined using two methods, low temperature by equilibration and high temperature by complete line-shape analysis. The low-temperature rates were obtained by dissolving crystalline **1** in CH_2Cl_2 at −70° and warming the sample

Table II

T, °C	*k*, sec^{-1}
−57	0.000169
−54	0.000453
−52	0.000711
16	1.67
24	5.81
34	10.3
36	24.8
47	54.6
48	58.7
51	70.4
54	116
57	141

(21) Calculated using data given in ref 3b.

(22) H. Kessler, *Angew. Chem.*, **79**, 997 (1967); *Angew. Chem., Int. Ed. Engl.*, **6**, 977 (1967).

(23) A. Reiker and H. Kessler, *Tetrahedron*, **23**, 3723 (1967).

(24) Calculated using data given in the following references: F. A. L. Anet and J. M. Osyany, *J. Amer. Chem. Soc.*, **89**, 352 (1967); F. A. L. Anet, R. D. Trepka, and D. J. Cram, *ibid.*, **89**, 357 (1967).

in the probe to the temperature at which the rate was to be measured. Between 20 and 30 100-Hz sweep-width spectra were measured over a period of up to 2 hr at each of three temperatures, −57, −54, and −52°. The relative concentrations were determined for each scan using both peak heights and integrated peak intensities obtained by cutting out peaks on Xerox copies of the spectra and weighing them. The resulting mole fractions and times were then fitted, using a double precision linear least-squares computer program, to the rate equation for a first-order reaction,

$$\frac{-K}{K+1}\ln\left[1 - X_B(1 + 1/K)\right] = kt$$

where K is the equilibrium constant, X_B is the mole fraction of the low-field isomer, and k is the rate constant for isomerization. The equilibrium constant used was obtained by extrapolation from a plot of equilibrium constant *vs.* temperature. The rates obtained were: $-57°$, $k = (1.69 \pm 0.05) \times 10^{-4}$ sec^{-1}, $-54°$, $k = (4.53 \pm 0.16) \times 10^{-4}$ sec^{-1}, and $-52°$, $k = (7.11 \pm 0.19) \times 10^{-4}$ sec^{-1}. The rates in the high-temperature region (16–57°) were determined by CLS. Arrhenius parameters obtained using high-temperature (16–57°) rates only were: $E_a = 19.4 \pm 0.8$ kcal/mol; $\log A = 15.0 \pm 0.6$ sec^{-1}; $\Delta H^{\ddagger} = 18.8 \pm 0.8$ kcal/mol; $\Delta S^{\ddagger} = 8 \pm 3$ eu. The correlation coefficient was −0.993. Arrhenius parameters obtained using both high- and low-temperature rates (−57 to 57°) were: $E_a = 16.2 \pm 0.3$ kcal/mol; $\log A = 12.8 \pm 0.2$ sec^{-1}; $\Delta H^{\ddagger} = 15.7 \pm 0.3$ kcal/mol; $\Delta S^{\ddagger} = -2 \pm 1$ eu. The correlation coefficient was −0.998. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated using the equations given below. The values obtained from the two methods for calculating $\Delta S^{\ddagger}$ were in good agreement: $\Delta H^{\ddagger} = E_a - RT$; $\Delta S^{\ddagger} = R\ln(Ah/k_bT) - R$; $\Delta S^{\ddagger} = (\Delta H^{\ddagger} - \Delta G^{\ddagger})/T$. The entropy and enthalpy of activation were also calculated using a linear least-squares computer program of the Eyring equation

$$\ln(k/T) = \ln(k_b/h) + \Delta S^{\ddagger}/R - \left(\frac{\Delta H^{\ddagger}}{R}\right)\left(\frac{1}{T}\right)$$

These results were identical with those obtained from Arrhenius parameters ($\Delta H^{\ddagger} = 15.6 \pm 0.3$ kcal/mol; $\Delta S^{\ddagger} = -1.6 \pm 1$ eu).

The Acid-Catalyzed Isomerization of *cis*-1-Phenyl-1,3-butadiene and *cis*-1-Methyl-3-phenylallyl Alcohol[1]

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Received June 25, 1970

Abstract: The kinetics of the acid-catalyzed isomerization of *cis*-1-phenyl-1,3-butadiene (**1**) and *cis*-1-methyl-3-phenylallyl alcohol (**2**) to the corresponding trans compounds in aqueous sulfuric acid as well as in 40% aqueous dioxane containing perchloric acid have been investigated. Both reactions give good pseudo-first-order kinetics, and plots of log k *vs.* $-H_0$ give good straight lines. The rate of isomerization of **1** in deuteriosulfuric acid is slower by a factor of 2.24–3.15 than in aqueous sulfuric acid, although deuterium incorporation occurs exclusively at the terminal carbon atom. The rate of isomerization of **2** is accelerated in deuteriosulfuric acid by a factor of 2.5 over the aqueous acid, and there is no deuterium incorporation into the molecule except for the hydroxyl proton. The loss of ^{18}O label from labeled **2** occurs at the same rate as isomerization to trans alcohol, indicating that the loss of water from protonated **2** is rate determining in the isomerization and there is no detectable return to starting material. Similarly, the protonation of **1** to give the cis carbonium ion is found to be rate determining. In each case, rapid rotation about the C_1–C_2 bond converts the cis carbonium ion directly to the trans ion before attack by solvent can occur. Thus, even under kinetic control, all products are derived from the trans carbonium ion. This is the first case of a cis allylic cation that is not stable with respect to cis–trans isomerization in aqueous solution. Due consideration to the energetic requirements is given in the discussion of these processes.

The present paper is a continuation of a kinetic and mechanistic study of the reactions of *cis*- and *trans*-1-phenyl-1,3-butadiene and their water adducts in aqueous acids.[4,5] It will be shown below that *cis*-1-phenyl-1,3-butadiene (**1**) and *cis*-1-methyl-3-phenylallyl alcohol (**2**) isomerize readily in moderately concentrated acids to give ultimately the same equilibrium mixture that is obtained from the corresponding trans compounds in the same media. A survey of the literature pertaining to such processes shows precedents for two types of behavior.

The cis–trans isomerization of allylic alcohols has been studied by Young and Franklin,[6] who followed the acid-catalyzed interconversion of α-methylallyl alcohol and *cis*- and *trans*-crotyl alcohols. They observed that starting from either isomer of crotyl alcohol the vapor phase chromatography (vpc) peak corresponding to α-methylallyl alcohol appeared before that of the other isomer, indicating that α-methylallyl alcohol is an intermediate in the isomerization. All three alcohols yielded the same product mixture (66.28% α-methylallyl alcohol, 24.46% *cis*-, and 3.73% *trans*-crotyl alcohol) under the same conditions. The rate of disappearance of each alcohol was followed by vpc, and on the basis of these rates a theoretical equilibrium distribution of products was calculated. The observed results agreed best with the product distribution predicted for the following mechanism. Thus, it was concluded that the *cis*- and *trans*-allylic carbonium ions are stable with respect to geometrical isomerization, a conclusion reached with other allylic systems.[7] By

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