Collection of the *Renilla reniformis*, preparation of the crude extract, and settlement assays were performed by Dr. D. Rittschof and A. R. Schmidt, Duke University. Single-crystal X-ray structure determinations were performed by Dr. S. R. Wilson at the University of Illinois.

Registry No. 1, 104715-93-7; 2, 104715-94-8; 3, 104715-95-9.

Supplementary Material Available: Description of the X-ray diffraction determination of 3, including final atomic positional parameters (Tables 3 and 4), thermal parameters (Table 5), and selected bond distances and bond angles (Table 6), (6 pages); observed and calculated structure factors (Table 7) (12 pages). Ordering information is given on any current masthead page.

Further Kinetic Evidence for the Competitive Rotational and Inversional *Z*–*E* Isomerization of Substituted Azobenzenes

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The first-order rate constant for thermal *Z*–*E* isomerization of 4-(dimethylamino)-4′-nitroazobenzene was measured in various solvents at different temperatures and pressures. The temperature dependence of the activation volume was qualitatively different in different solvents. The Arrhenius plots were linear for ethanol and methanol but deviated upward at high temperatures for benzene and dioxane. These results unequivocally indicate that there are two competing reaction mechanisms in the *Z*–*E* isomerization of the azobenzene.

It is generally agreed that the thermal *Z*–*E* isomerization of azobenzenes proceeds through a transition state in which one of the nitrogen atoms is sp-hybridized. This mechanism is usually called "inversion". Conclusive experimental evidence for the inversion mechanism is the facile isomerization of an azobenzene unit incorporated into a ring system[1,2] in which the rotation of the phenyl ring around the nitrogen–nitrogen bond is extremely difficult for steric reasons. The decrease in polarity during activation[3,4] and the absence of a solvent effect on the activation parameters[5] are also in accord with the inversion mechanism. Theoretical calculations also provide support for inversion.[6,7]

In a previous report,[8] it was concluded that the thermal *Z*–*E* isomerization of *p*-aminoazobenzenes proceeds by two routes as shown in Scheme I. Inversion about a nitrogen atom effects isomerization via the activated complex **1**. In the route via **2**, the nitrogen–nitrogen π-bond is ruptured heterolytically, and rotation around the remaining σ-bond gives the *E* isomer (rotation mechanism). This conclusion was based mainly on the effects of solvent and pressure on the isomerization kinetics of several substituted azobenzenes. For example, the isomerization rate of 4-(dimethylamino)-4′-nitroazobenzene (NMe_2-NO_2-AB) increased rapidly with increasing polarity of the reaction medium. These results seem to reflect a large polarity increase during activation, and for this reason the dipolar transition state **2** was proposed.

Recently, Nishimura et al.[9] proposed that the isomerization of push–pull substituted azobenzenes in polar solvents proceeds by a single path through the intermediate resonance hybrid **3** (Chart I). Their proposal was based mainly on a correlation between the absorption maxima of the ortho-substituted *E* isomers of NMe_2-NO_2-AB and their free energies of activation for the *Z*–*E* isomerization. They took this correlation to indicate coplanarity of the two phenyl rings in the transition state and concluded that the nonplanar transition state **2** is not compatible with their observations. They also measured the reaction volumes for the isomerization in relatively nonpolar solvents[10] and found that the reaction volume was slightly

Scheme I

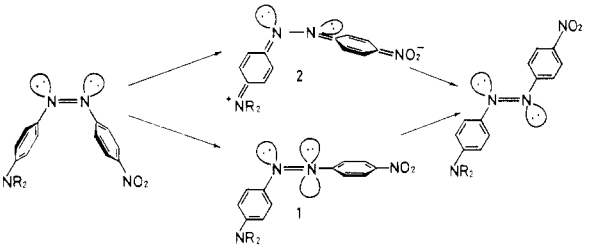
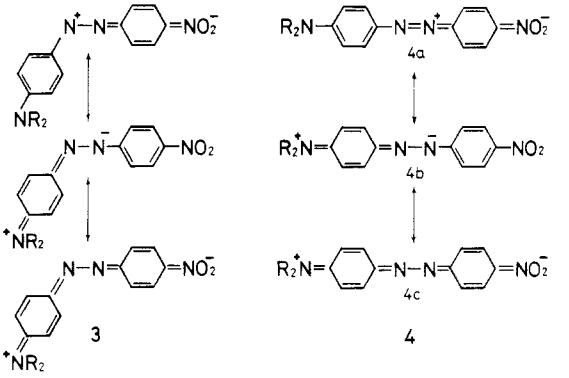


Chart I



(1) Asano, T.; Okada, T.; Shinkai, S.; Shigematsu, K.; Kusano, Y.; Manabe, O. *J. Am. Chem. Soc.* **1981**, *103*, 5161.
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(5) Otruba, J. P.; Weiss, R. G. *J. Org. Chem.* **1983**, *48*, 3448.
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(9) Nishimura, N.; Kosako, S.; Sueishi, Y. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1617.
(10) Tanaka, T.; Sueishi, Y.; Yamamoto, S.; Nishimura, N. *Chem. Lett.* **1985**, 1203.

0022-3263/86/1951-4454$01.50/0

Chart II

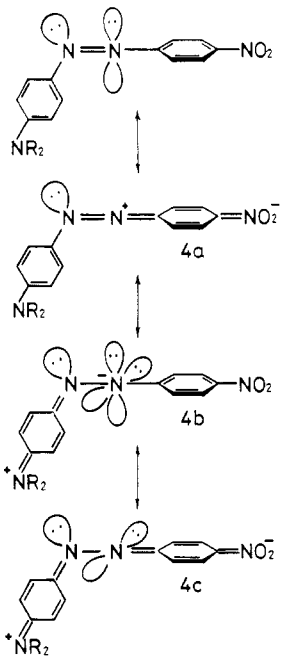
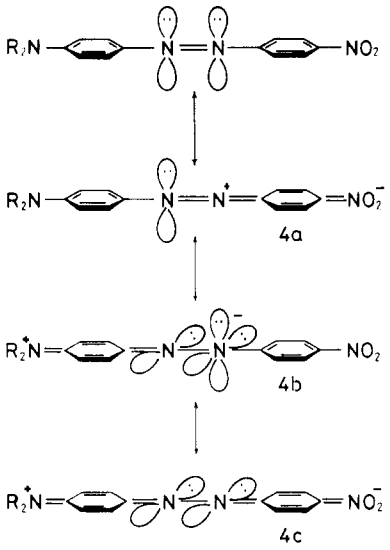


Chart III



larger than the activation volume. According to Nishimura, this fact suggests that the transition-state polarity is smaller than that of the *E* isomer and can only be explained by the planar inversional transition state **3**. However, as pointed out by Whitten,[11] a correlation between the absorption maxima and the rate constants suggests that the transition state is zwitterionic, as is the excited state, but it does not require that the two phenyl groups be coplanar in the transition state. Accordingly, transition state **2** is not incompatible with this correlation. The less negative activation volume is also compatible with Scheme I. In nonpolar solvents, the reaction must be mostly inversional, and as can be seen from high pressure studies of unsubstituted and symmetrically substituted azobenzenes,[1] the activation volume for inversional isomerization is close to zero. Therefore, if the reaction proceeds predominantly via the inversion path, it is natural to observe activation volumes that are smaller than the volume change of the reaction. In summary, the experimental facts given by Nishimura are compatible with Scheme I.

Bellobono et al.[12] have proposed that the resonance hybrid **4** is the activated complex intermediate on the basis of solvent effects on the isomerization kinetics of 4-(diethylamino)-4′-methoxyazobenzene (NEt_2-MeO-AB) and NE_2-NO_2-AB. They measured the rate constants in ten aprotic solvents. Although the magnitude of the solvent effect was much different for these two azobenzenes, both responded similarly to polarity change, i.e., the rate increased with increasing polarity of the solvent. Bellobono analyzed the results with Taft's π^* values[13] and concluded that "the same type of process takes place in going from the initial to the activated state" in both compounds. In NEt_2-MeO-AB, the methoxy group diminishes electron donation by the amino group, and the mechanism is almost certainly inversion. The much larger transition-state polarity in NEt_2-NO_2-AB was assumed to reflect the intermediate dipolar and planar inversion transition state **4**.[14] Although the authors state that the differences in the solvent effects for NEt_2-MeO-AB and NEt_2-NO_2-AB "seem to be more quantitative than qualitative", the effect is more than 33 000 times larger for the latter when the rates in hexane and in dimethyl sulfoxide are compared. Therefore, it is not unreasonable to assume two different mechanisms for these compounds.

In order to resolve the differences in interpretation between Nishimura and Bellobono and ourselves,[8] we decided to undertake further kinetic measurements on NMe_2-NO_2-AB.

In the Nishimura–Bellobono single-path mechanism (inversion only), the increased polarity of the transition state is ascribed to the contribution of the inversional dipolar resonance structures. In our mechanism (inversion–rotation, Scheme I), it is attributed to an increased proportion of rotational isomerization. If Scheme I is correct, the reaction should be almost pure rotation in polar solvents because there is little reason to expect large acceleration of inversion by electrostatic solute–solvent interactions. In fact, the isomerization of azobenzene is slightly retarded as the solvent polarity increases.[1,15–18] In hexane, however, the activation energy for inversion should be slightly lower, judging from the activation volume. The activation volume at 40 °C increases from −3.0 mL/mol in hexane to −10.9 in carbon tetrachloride to −22.0 in benzene. Since a slight increase in solvent polarity results in a large negative activation volume, the activation energy difference between the two routes cannot be large in hexane. Therefore, there should be solvents in which the

(11) Schanze, K. S.; Mattox, T. F.; Whitten, D. G. *J. Org. Chem.* **1983**, *48*, 2808.

(12) Marcandalli, B.; Pelliciari-Di Liddo, L.; Di Fede, C.; Bellobono, I. R. *J. Chem. Soc., Perkin Trans. 2* **1984**, 589.

(13) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027.

(14) In **4a**, the nitrogen atom on the right must be sp-hybridized because it is the central atom of a cumulative double bond. Thus the 2p orbitals of the right-hand phenyl ring must be perpendicular to the π-bond between the nitrogens, and this ring and the nitrogens in the same plane. Since the authors claim coplanarity of the two phenyl rings, their 2p orbitals have to be perpendicular to the π-bond between the nitrogens. On the other hand, in **4b,c** the 2p orbitals of the nitrogens and the left-hand phenyl ring must be parallel. Therefore, **4a–c** cannot be resonance hybrids. To avoid this contradiction, it is necessary either that the two phenyl rings be mutually perpendicular (Chart II) or that both nitrogen atoms be sp-hybridized (Chart III).

(15) Hartley, G. S. *J. Chem. Soc.* **1938**, 633.

(16) Halpern, J.; Brady, G. W.; Winkler, C. A. *Can. J. Res.* **1950**, *28B*, 140.

(17) Hoffmann, H.-J. *Z. Chem.* **1979**, *19*, 424.

(18) The inversional rate increases somewhat with solvent polarity when an electron-donating or -attracting substituent is present. However, the effect is several orders smaller than in NMe_2-NO_2-AB.

Table I. Temperature Dependence of the Activation Volume at Zero Pressure (mL/mol) for Thermal *Z*-*E* Isomerization of 4-(Dimethylamino)-4'-nitroazobenzene in Various Solvents

	T, °C						
solvent	10	25	30	40	50	60	70
hexane				−3.02[a]	−3.68[a,b]		−7.70[c]
benzene			−23.81[a]	−22.00[a]	−19.85	−19.48	−19.36[a]
1,4-dioxane				−17.52	−19.92	−17.64	−19.06
THF	−23.68	−28.14		−29.35	−31.68	−33.45	
o-$Cl_2C_6H_4$	−20.62	−21.65		−22.29			
ethanol	−21.19	−22.93		−25.61		−28.53	−31.22
methanol	−23.01	−25.46	−26.72	−27.62		−30.39	

[a] From ref 8. [b] At 55 °C. [c] Recalculated from the rate constants in ref 8.

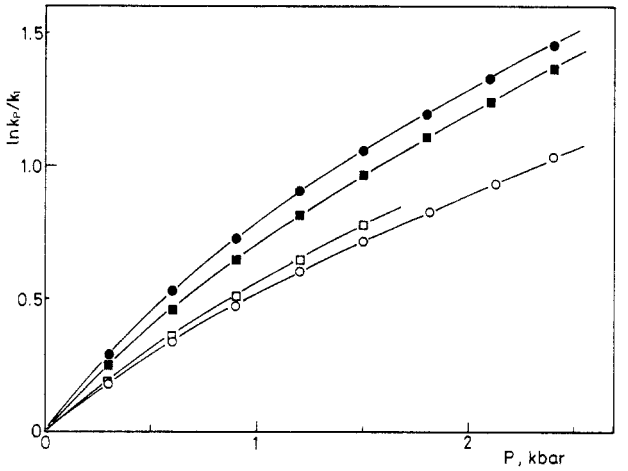


Figure 1. Temperature dependence of the pressure effect on the thermal *Z*-*E* isomerization of 4-(dimethylamino)-4'-nitroazobenzene in 1,4-dioxane and ethanol: (□) dioxane at 40 °C; (○) dioxane at 70 °C; (■) ethanol at 10 °C; (●) ethanol at 70 °C.

activation energy is a little lower for rotation but where the rotational isomerization is not predominant. Thus the temperature dependence of the activation volume should depend on solvent polarity. In polar solvents, it should be the same as in other polar reactions. In the same solvent, the effect of electrostrictive volume contraction is larger at higher temperatures. For example, the ionization volumes of organic and inorganic acids and bases become larger at higher temperatures.[19-23] Therefore, in methanol and other polar solvents, the activation volume should become larger at higher temperatures. In hexane, an increase in temperature should cause an increase in the proportion of rotation because of its higher activation energy, resulting in a larger activation volume. On the other hand, the opposite temperature effect would be expected in benzene because the activation energy for inversion might be slightly higher in this solvent. If this is the case, a higher temperature should cause an increased proportion of inversion and a smaller activation volume. In short, the temperature dependence of the activation volume in various solvents must be qualitatively different if there are two competing reactions.

This conclusion is in marked contrast to that expected for the mechanism of Nishimura and Bellobono. If the reaction proceeds only via the inversional path, the temperature dependence of the activation volume should be much simpler. In hexane, the activation volume should be almost independent of temperature because there would be essentially no increase in electrostriction during activation. In other solvents, $-d\Delta V^{\ddagger}/dT$ should be positive because electrostriction causes a larger contraction at higher temperatures.

There is one more factor. If there are two reactions with different activation energies, the Arrhenius plots should deviate upward at high temperatures. If there is only one reaction path, a linear Arrhenius plot should be obtained in all solvents. Thus, determination of the rate constants at various temperatures and pressures should distinguish between the two mechanisms.

Temperature Dependence of the Activation Volume. The effects of pressure on the first-order rate constant were measured in various solvents at different temperatures. All results except those in hexane at 40 and 55 °C[24] gave smoothly curved plots of ln *k* against pressure (Figure 1, Table I). The parameters in eq 1[25] were determined by nonlinear least-squares analysis, and the activation volumes at zero pressure were determined by eq 2. For the results in hexane at 40 and 55 °C, eq 3 and

$$\ln \frac{k_p}{k_1} = aP + b \ln (1 + cP) \quad (1)$$

$$\Delta V_0^{\ddagger} = -(a + bc)RT \quad (2)$$

4 were adopted. The activation volume obviously in-

$$\ln \frac{k_P}{k_1} = a + bP \quad (3)$$

$$\Delta V_0^{\ddagger} = -bRT \quad (4)$$

creases with temperature in the polar solvents methanol and ethanol. This effect must be the result of increased electrostriction and could be explained by either mechanism. The same effect was observed in tetrahydrofuran and *o*-dichlorobenzene, indicating the importance of electrostriction in these moderately polar solvents. However, in hexane the increase in activation volume with temperature can hardly be explained by the inversion-only mechanism because the activation volume at 40 °C indicates no increase in electrostriction during activation. On the other hand, this result can be explained by a slight increase in the rotational proportion in Scheme I. The activation volume for pure rotation in hexane must have a large negative value,[8] and only a few percent increase in rotation would suffice to give the observed activation volume at 70 °C. Furthermore, the decrease in activation volume with increasing temperature in benzene cannot be explained by an inversion-only mechanism. In such a mechanism, the inversion transition state in benzene must have relatively large polarity because the activation volume has a large negative value, and $\Delta V^{\ddagger}$ should be more negative at higher temperatures. On the other hand, if rota-

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(20) Sretenskaya, N. G. *Geokhimiya* **1977**, 430.
(21) Read, A. J. *J. Solution Chem.* **1975**, *4*, 53.
(22) Read, A. J. *J. Solution Chem.* **1982**, *11*, 649.
(23) Inoue, H.; Hara, K.; Osugi, J. *Rev. Phys. Chem. Jpn.* **1978**, *48*, 44.

(24) Since the rate in hexane is low at these temperatures, the measurement had to be done in a few minutes and reproducibility was poor.
(25) Asano, T.; Okada, T. *J. Phys. Chem.* **1984**, *88*, 238.

Table II. First-Order Rate Constants (k, s^{-1}) for the Z–E Isomerization of 4-(Dimethylamino)-4′-nitroazobenzene at 1 bar in Various Solvents

	T, °C						
solvent	10	25	30	40	50	60	70
hexane		0.00201[a]		0.0107[a]	0.0450[a,b]		0.159[a,c]
benzene		0.0108[a]	0.0178[d]	0.0429[e]	0.1089	0.2533	0.578[a]
1,4-dioxane		0.0142[a]		0.0512	0.1145	0.2572	0.561
THF	0.191	0.513		1.303	2.376	4.221	
o-$Cl_2C_6H_4$	0.230	0.692		1.963			
ethanol	5.90	17.39		45.46		141.3	238.3
methanol	16.51	47.03	64.71	119.0		368.4	

[a] From ref 8. [b] At 55 °C. [c] At 50 bar. [d] From ref 26. [e] From ref 4.

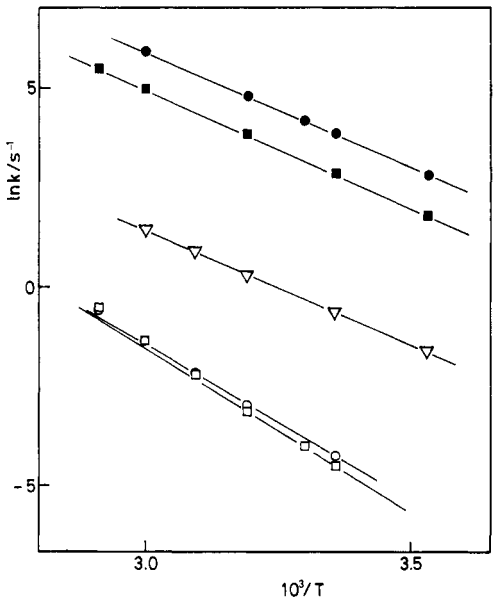

Figure 2. Arrhenius plots for the thermal Z–E isomerization of 4-(dimethylamino)-4′-nitroazobenzene in various solvents at 1 bar: (□) benzene; (○) dioxane; (▽) tetrahydrofuran; (■) ethanol; (●) methanol.

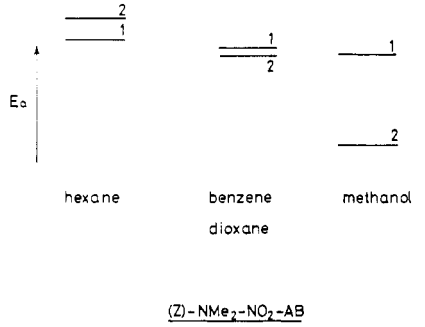

Figure 3. Schematic illustration of the relative energies of the rotational and the inversional transition states in solvents with different polarities.

tion and inversion are competing as in Scheme I, the proportion of inversion should increase with increasing temperature in benzene and the activation volume should decrease.

The reason for the apparent independence of activation volume on temperature in dioxane can also be found in Scheme I. If the effect of increased electrostriction is offset by an increase in the proportion of inversion, nearly the same activation volumes should be observed at different temperatures. The inversion-only mechanism predicts a larger activation volume at higher temperatures in this solvent. The results in Table I are, therefore, compatible with Scheme I but not with an inversion-only mechanism.

Arrhenius Plots. Table II presents the first-order rate constants at 1 bar in various solvents, and Figure 2 shows the Arrhenius plots. Good linear plots were observed for methanol and ethanol over a wide range of temperature. For hexane, because of the relatively large experimental errors,[24] it was impossible to draw a conclusion as to linearity. However, for benzene and dioxane, in which the activation energy for rotation is expected to be slightly lower, the plots deviate from linearity at 60 and 70 °C.

Table III. Comparison of Extrapolated and Observed Rate Constants

		60 °C		70 °C	
solvent		k_{calcd}	k_{obsd}	k_{calcd}	k_{obsd}
benzene	(25–50 °C)[a]	0.242	0.253	0.528	0.578
1,4-dioxane	(25–50 °C)	0.241	0.257	0.489	0.561
ethanol	(10–40 °C)	144	141	245	238
methanol	(10–40 °C)	364	368		

[a] Temperature range used for the calculation.

The observed and calculated rate constants are compared in Table III. In benzene and dioxane, the calculated rate constants on the basis of the rates between 25 and 50 °C are much smaller than the experimental values. The extrapolated values in the alcohols are in good agreement with those observed. The plot for tetrahydrofuran seems to deviate a little at 60 °C but is inconclusive. These results, especially the upward deviations in benzene and dioxane, strongly suggest the validity of Scheme I. If there is only one reaction path, it is difficult to understand the observation of nonlinear plots in only these two solvents. Since the reaction is a unimolecular single-step reaction of a neutral solute, it is hard to imagine other reasons for the positive value of the heat capacity of activation observed only in relatively nonpolar solvents.

Conclusions

The solvent dependence of the sign of $d\Delta V^{\ddagger}/dT$ and the nonlinear Arrhenius plots for benzene and dioxane are compatible with the competitive rotation–inversion reaction of Scheme I, but they cannot easily be explained by a single-path mechanism. All the observations can be explained if it is assumed that the relative height of the transition-state energy varies with solvent as schematically illustrated in Figure 3.

Experimental Section

Materials. Commercial NMe_2-NO_2-AB (mp 234–235 °C, lit.[27] mp 232–234 °C) was used after recrystallization. Solvents were spectrophotometric or "guaranteed reagent" grade (Wako Pure Chemical Ind.) and were distilled before use.

Kinetic Measurements. All rate constants were measured by flash spectroscopy; details are described elsewhere.[4,8] The high-pressure optical vessel was similar to that described in ref 25. The diameters of the windows for the xenon flash bulb and

(26) Asano, T. *J. Am. Chem. Soc.* **1980**, *102*, 1205.
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the monitoring light were 18 and 9 mm, respectively. The inner cell was a glass bulb with a 0.5-mm i.d. capillary tube; the bulb diameter was kept below 17 mm. Pressure was measured with a Heise Model CM bourdon tube gage with a full scale of 60 000 psi. The temperature was kept constant (±0.05 °C) by circulating thermostatted water through an outer jacket that covered the whole vessel.

Registry No. 4-(Dimethylamino)-4'-nitroazobenzene, 2491-74-9.

Supplementary Material Available: Tables of rate constants for the *Z-E* isomerization of NMe_2-NO_2-AB in various solvents and at various temperatures and pressures (6 pages). Ordering information is given on any current masthead page.

Acid-Catalyzed Reactions of Ortho-Substituted Benzohydroxamic Acids in Polyphosphoric Acid (PPA)

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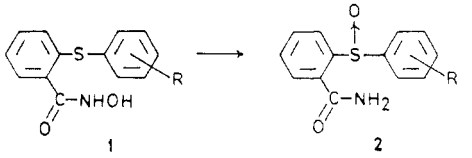
Ortho-substituted benzohydroxamic acids undergo a variety of reactions when treated with PPA. The nature of substituents on the ring and on the functional group CONHOH plays a key role in influencing the reaction pathways. The difference in behavior may arise due to change in site of protonation depending upon the substitution. However, no clear-cut relationship could be established as attempts to monitor reactions on NMR proved inconclusive.

The site of protonation in hydroxamic acids has been the subject matter of several publications.[1-5] ^1H NMR analysis seems to have provided definite clues as to the site of protonation in hydroxamic acids. Lobo and coworkers[5] have shown that in case of *N*-methylhydroxamic acids nature of protonation depends inter alia on the concentration of the acid employed. Using the ^1H NMR data they have shown that at moderate concentration of acid the carbonyl oxygen is protonated whereas at higher concentrations of acid the nitrogen atom is protonated. These findings are congruent with the earlier reports. It should be noted, however, that there are no reports on hydroxyl oxygen of hydroxamic acid being protonated.

The rearrangement of 2-(arylthio)benzohydroxamic acid (**1**) to 2-(arylsulfinyl)benzamide **2** (eq 1) occurs in polyphosphoric acid (PPA) and also in trifluoroacetic acid.[6]

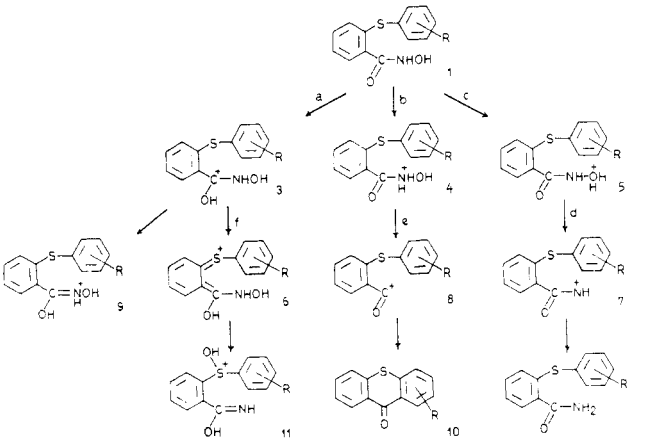


1 2 (1)

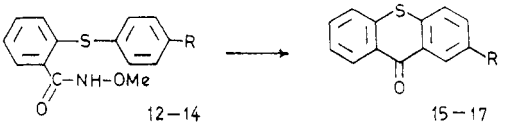
Attempts to monitor the rearrangement of **1** to **2** in deuteriated TFA by using ^1H NMR spectroscopy met with little success. We have been able to observe the emergence of a broad multiplet at δ 8-8.2, presumably the NH signal of the product whose peak area matches with the progress of the reaction.

In the absence of any possibility of direct evidence on the site of protonation coupled with our own experience investigating acid-catalyzed reactions, it was thought worthwhile to search for indirect evidence for the site of protonation by chemical transformations of these protonated species. 2-(Arylthio)benzohydroxamic acids constitute an interesting system wherein the site of protonation varies with substitution and chemical consequences of this variation lead to different products.

Scheme I



Scheme II



R
12,15 : H
13,16 : Me
14,17 : OMe

There are three possible sites of protonation in 2-(arylthio)benzohydroxamic acid, viz., (i) carbonyl oxygen, (ii) nitrogen, and (iii) hydroxyl oxygen. Each of these would lead to different cleavage products or tautomers as shown in Scheme I. It is reasonable to assume that rearrangement of **1** (eq 1) would proceed either from **6** or **9**. Pathway d on the other hand generates corresponding amide and highly improbable oxonium species (^+OH).

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