attack on the tetramethyl compound 4 is favored both by orbital energy (i.e., the energy of the HOMO) and electrostatic interactions. In contrast, electrophilic attack on the phenyl-substituted derivatives involves attack on the lower energy second OMO[12] resulting in a slower reaction, the position of attack being governed by electrostatic interactions. In these cases the electrostatic interaction energy term dominates the attractive bonding interaction energy terms, whose magnitude is inversely proportional to the orbital energy.

Experimental Section

General Conditions for Reactions of Alkenylidenecyclopropanes with Trichloroacetic Acid. To a solution of 0.25 mequiv of the alkenylidenecyclopropane in 0.50 mL of carbon tetrachloride in an NMR tube was added 0.25 mequiv of trichloroacetic acid (TCA) in 0.10 mL of carbon tetrachloride. The solution was rapidly mixed and immediately placed in the NMR probe. The NMR spectrum was periodically integrated over a region containing only characteristic peaks of the starting alkenylidenecyclopropane (~5 s elapsed time from mixing to recording of first integral scan). The percent unreacted alkenylidenecyclopropane was plotted vs. time and $t_{1/2}$ taken as the time corresponding to 50% reaction. In all cases, the reactions proceeded to >95%.

Reaction of 1 with TCA. The final NMR spectrum at >95% reaction showed the presence of adducts **8** and **9**, which were separated by high-pressure liquid chromatographic techniques on a 2 ft × $^3/_8$ in. Corasil column using hexane as eluent.

8: NMR ($CDCl_3$, ^1H FT spectrum on pure fraction isolated by HPLC, integral from CW spectrum of mixture of 8 and 9) δ 1.77 (overlapping d's, J's = 2.2 and 1.6 Hz, 6 H), 4.95 (s, 2 H), 5.79 (br s, 1 H), 6.62 (br s, 1 H), 7.30 (m, 5 H); MS calcd for $C_{15}H_{15}{}^{35}Cl_3O_2$ 332.0137, obsd 332.0137.

9: NMR ($CDCl_3$) δ 1.38 (dd, J's = 10.6, 6.1 Hz, 1 H), 1.44 (s, 6 H), 1.75 (dd, J's = 8.1, 6.1 Hz), 2.56 (dd, J's = 10.6, 8.1 Hz, 1 H), 5.32 (br s, 1 H), 7.25 (br s, 5 H); MS calcd for $C_{15}H_{15}{}^{35}Cl_3O_2$ 332.0137, obsd 332.0144.

NMR spectra recorded early during the reaction indicated the presence of 7 (br s; at δ 5.11 and 5.46) which on longer reaction times is converted to **8**.[2] Integration of NMR spectra taken after low conversions indicate that **7**, **8**, and **9** are initially formed in a 2:4:1 ratio.

Reaction of 10 with TCA. NMR spectra recorded after short reaction times clearly showed the presence of **11** and **12** (>9:1 ratio), and possibly very small quantities of the isomer of **11** (corresponding to **7** formed from **1**). NMR spectra recorded later in the reaction showed the presence of other components (unidentified) and decreasing quantities of **11** and **12**. Attempts to isolate pure samples of **11** and **12** were not successful. 11: NMR ($CDCl_3$, from a mixture of 11 and 12) δ 1.70 (br s, 3 H), 1.83 (overlapping d's, $J \approx 1.2$ and 2.1 Hz, 6 H), 4.74 (s, 2 H), 5.75 (br s, 1 H), 7.30 (m, 5 H). 12: NMR δ 1.52 (s, 3 H), 1.63 (s, 6 H), 5.11 (br s, 1 H), 7.3 (m, 5 H). The ring methylene hydrogens of **11** and **12** appear as poorly resolved multiplets partially obscured by the methyl resonances of **11** and **12**.

Reaction of 13a and 13b with TCA. The NMR spectrum of the product derived from both **13a** and **13b** showed the presence of a single adduct, **14**: NMR ($CDCl_3$) δ 1.34 (d, J = 1.8 Hz, 3 H), 1.53 (d, J = 6.7 Hz, 3 H), 1.77 (d, J = 1.3 Hz, 3 H), 5.57 (q, J = 6.7 Hz, 1 H), 5.83 (m, 1 H), 6.65 (m, 1 H), 7.3 (br s, 5 H); MS calcd for $C_{16}H_{17}{}^{35}Cl_3O_2$ 346.0294, obsd 346.0288.

Reaction of 15a and 15b with TCA. The reaction of **15a** and **15b** with TCA produced a mixture whose NMR spectrum was very complex and could not be interpreted. No resonance in the δ 5.8 region ($-CH{=}C(CH_3)_2$) could be detected. Although the initial reaction was complete in ~1 min, the NMR spectrum of the product mixture continued to change. After 5 min a substantial portion of the initially formed product had disappeared.

Reaction of 4 with TCA. The reaction of **4** with TCA immediately produced a mixture of **18** and **19** in an approximate 1:1 ratio. Product **18** was identified by comparison of ^1H chemical shifts previously observed.[2] Product **19** was identified by comparison of the ^1H chemical shifts with the corresponding acetate previously characterized,[2] all chemical shifts corresponding to ±0.01 ppm. In addition to **18** and **19** a minor product appears to have been formed, as evidenced by the appearance of two methyl singlets in the NMR. This adduct could not be isolated and it is not known whether this adduct is a primary or secondary product.

Registry No.—**7**, 62861-82-9; **8**, 62861-83-0; **9**, 62861-84-1; **11**, 62861-85-2; **12**, 62861-86-3; **14**, 62861-87-4; trichloroacetic acid, 76-03-9.

References and Notes

(1) D. J. Pasto, A. F.-T. Chen, G. Ciurdaru, and L. A. Paquette, *J. Org. Chem.*, **38**, 1015 (1973).
(2) D. J. Pasto and M. F. Miles, *J. Org. Chem.*, **41**, 425 (1976).
(3) Although CSI and benzenesulfenyl chloride offered certain advantages in such a kinetic study, it was highly desirable to use an electrophilic reagent which did not add via a possible concerted process[1] or via an onium ion intermediate.[2]
(4) Calculated on the basis of 95% situselectivity (assumed limits of NMR detectability of product formation) in the aryl- and alkyl-substituted cases. An assumed 99% situselectivity would yield a reactivity difference of >300 000.
(5) The formation of ring-retained products from **1** and **10** differs from earlier observations in which only ring-opened products were formed.[1,2] The formation of ring-retained products probably occurs via concerted addition pathways which are competitive with cation intermediate pathways in the less polar solvent carbon tetrachloride.
(6) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); *Nature (London)*, **159**, 167, 712 (1947).
(7) M. Hanack, T. Bässler, W. Eymann, W. E. Heyd, and R. Kopp, *J. Am. Chem. Soc.*, **96**, 6686 (1974).
(8) D. J. Pasto, T. P. Fehlner, M. E. Schwartz, and H. F. Baney, *J. Am. Chem. Soc.*, **98**, 530 (1976).
(9) C. F. Wilcox, L. M. Loew, and R. Hoffmann, *J. Am. Chem. Soc.*, **95**, 8193 (1973).
(10) In other studies, replacement of a phenyl by vinyl causes only minor changes in wave function energies or coefficients and significantly reduces computing time.
(11) See A. Devaquet and L. Salem, *J. Am. Chem. Soc.*, **91**, 3793 (1969).
(12) A reaction involving a lower energy second OMO instead of involving the HOMO has been previously reported. See: M. Arbelot, J. Metzger, M. Chanon, G. Guimon, and G. Pfister-Guillouzo, *J. Am. Chem. Soc.*, **96**, 6217 (1974).

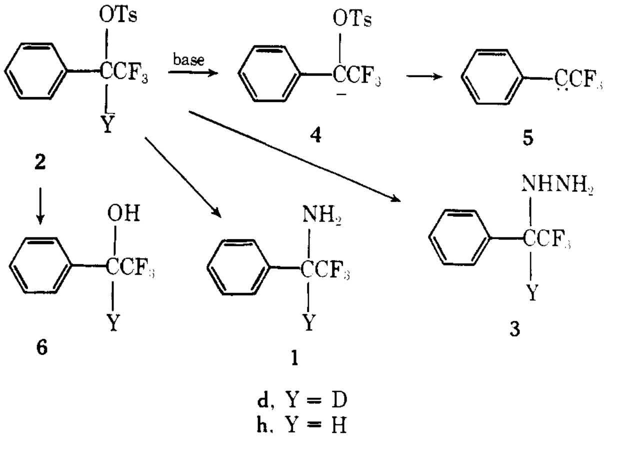
High Pressure Assisted Synthesis. Evidence for Nucleophilic Displacement on 2,2,2-Trifluoro-1-phenylethyl Tosylate

W. H. Pirkle,* J. R. Hauske, C. A. Eckert, and B. A. Scott

The Roger Adams Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

Received March 8, 1977

While searching for a practical synthesis of 2,2,2-trifluoro-1-phenylethylamine[1] (**1h**), we contemplated the report[2] that 2,2,2-trifluoro-1-phenylethyl tosylate (**2h**) reacts with hydrazine to afford the alkylated hydrazine **3h**. Trifluoromethyl groups severely impede S_N1 or S_N2 reactions when α to the reaction site.[3a–b] However, the hydrazinolysis reaction might conceivably proceed via attack upon hydrazine by the electrophilic carbene **5**, formed from α elimination of tosylate ion from carbanion **4**.



d, Y = D
h, Y = H

Comparative reactions show that tosylate **2h** is essentially inert to ammonia under conditions which cause complete hydrazinolysis.[4] However, at 6 kbar pressure the tosylate reacts smoothly with ammonia in dry THF (saturated at 0 °C, 1 atm) within 4 h at 130 °C to afford amine **1h** as the major product (>95%) with <2% of alcohol **6h** also formed. Alcohol **6h** may arise either from traces of water present or from attack by ammonia at sulfur. High pressure facilitates reactions developing charge separation in the transition state by enhancing solvent of the charged species (i.e., "electrostriction").[5]

To determine whether chiral amine results from chiral tosylate and to provide additional mechanistic information, chiral deuterated tosylate **2d** was similarly treated and found to afford racemic nondeuterated amine **1h.** Shorter reaction times allowed recovery of residual tosylate, which was found to have lost essentially all of its deuterium, as judged from ^{19}F NMR.[6] Addition of water to the reaction reduces the rate of the exchange reaction relative to that of the ammonolysis reaction.[7] For example, heating (*R*)-(−)-deuteriotosylate **2d,** $[\alpha]^{25}{}_{D}$ −54.5° (*c* 3.9, $CHCl_3$), prepared from enantiomerically pure deuterated (*R*)-(−)-carbinol, with ammonia dissolved in 90:10 THF–H_2O at 130 °C and 6 kbar pressure for 4 h converts 54% of the tosylate into a 61:39 mixture of nondeuterated–deuterated amine **1** and 5.8% into a 62:38 mixture of nondeuterated–deuterated alcohol **6.** The residual tosylate (40.2%) contains but 4% of the original deuterium. The isolated amine has $[\alpha]^{25}{}_{D}$ +9.2° (*c* 12.0, ethanol), 38% of the value reported for enantiomerically pure *S* amine **1h.**[1] Examination of the 90-MHz NMR spectrum of the isotopic mixture of amines **1h–d** using (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol[8] as a chiral solvating agent shows the protonated amine **1h** to be racemic. Therefore, deuterated amine **1d** must be essentially enantiomerically pure and configurationally inverted with respect to its tosylate precursor. Isolated alcohol **6** has $[\alpha]^{25}{}_{D}$ +12.9° (neat), 31% of the magnitude of the value reported[9] for the *S*-(+) enantiomer, $[\alpha]^{25}{}_{D}$ 41.2° (neat). Examination of the ^{1}H and ^{19}F NMR spectra of this alcohol in the presence of (*R*)-(+)-1-(1-naphthyl)ethylamine shows[10] the protonated alcohol to be racemic and the deuterated alcohol to be of high enantiomeric purity.[11] The recovered tosylate exhibits $[\alpha]^{25}{}_{D}$ − 1.61° (*c* 3.9, $CHCl_3$), which corresponds to 2.9% of its original value. It should be noted that the preparation of tosylate **2d** from alcohol **6d** proceeds *without* loss of deuterium. Thus, **2d** is of the same enantiomeric purity as its alcohol precursor. This alcohol, resolved via the large scale chromatographic separation of its diastereomeric (*R*)-(+)-1-(1-naphthyl)ethylamine carbamates,[12,13] showed no resonances attributable to the second enantiomer when its spectrum was determined in (*R*)-(+)-1-(1-naphthyl)ethylamine.[10] Thus, alcohol **6d** was enantiomerically pure within experimental limits. Control experiments show amine **1d** and alcohol **6d** to be configurationally stable under the ammonolysis conditions.

On the basis of the preceding results, it can be stated that, within the accuracy of the NMR measurements and the assumption that the deuterated and nondeuterated amines have essentially the same specific rotation, the major portion of amine **1** has arisen by ammonia displacement of tosylate ion with inversion of configuration. Owing to the accompaniment of the relatively fast tosylate exchange–racemization reaction, the question as to whether any of amine **1** has resulted from a carbene process is still moot. However, we have detected (^{19}F NMR) no product which might arise from reaction of carbene with solvent. Moreover, while the first step in the formation of carbene **5** is likely to be enhanced by increased pressure, since charge is formed, the overall process for carbene formation should be disfavored at high pressure. Presumably, the transition state for the fragmentation of anion **4** would involve an increase in volume and a loss of electrostriction owing to the greater electron delocalization in tosylate ion than in anion **4.** Finally, it is also evident that the presence of water gives rise to alcohol **6** by a process similar to that involved in ammonolysis, but possibly mitigated to a small extent by displacement at sulfur.

Experimental Section

Melting points were taken on a Buchi apparatus and are uncorrected. Infrared spectra were obtained with a Beckman IR-12 or a Perkin-Elmer 237B spectrophotometer. Proton and fluorine NMR spectra were obtained with Varian Associates A-60A, EM-390, HA-100, or HR-220 instruments. Mass spectra were determined using a Varian MAT CH-5 spectrometer. Microanalyses were performed by Nemeth and his colleagues.

All compounds in this study have been previously reported in the nondeuterated forms. The deuterated compounds were prepared as follows.

2,2,2,-Trifluoro-1-deuterio-1-phenylethanol (6d). Sodium borodeuteride[15] was added portionwise to a solution of 2,2,2-trifluoroacetophenone (5.9 mmol, 1.03 g) in dry methanol (25 mL) until such addition no longer produced an exothermic reaction. After the reaction mixture cooled to room temperature, it was diluted with 25 mL of water, washed with 30 mL of 3 M HCl, and extracted with two 50-mL portions of methylene chloride. The combined extracts were dried over anhydrous magnesium sulfate and concentrated, and the crude alcohol distilled [bp 92 °C (15 mm)] to afford **6d** in 96% yield: NMR ($CDCl_3$) δ 3.68 (br s, OH), 7.42 (br s, C_6H_5); IR (neat) 3450 (OH), 1250, 1150, 1050, 1000 (CF_3) cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 177 (40, M^+).

Anal. Calcd for $C_8H_6DF_3O$: C, 54.24; H, 3.41. Found: C, 54.19; H, 3.29.

Resolution of (*R*)-(−)-2,2,2-Trifluoro-1-deuterio-1-phenylethanol (6d). Deuterated carbinol **6d** was converted to the diastereomeric (*R*)-(+)-1-(1-naphthyl)ethylamine carbamates, which were chromatographically separated as previously described.[12,13] The appropriate diastereomerically pure carbamate was converted with refluxing sodium ethoxide–ethanol into enantiomerically pure (*R*)-(−)-deuteriocarbinol **6d,** $[\alpha]^{25}{}_{D}$ −41.09° (neat) with no apparent deuterium loss (NMR).

(*R*)-(−)-2,2,2-Trifluoro-1-deuterio-1-phenylethyl tosylate (2d) was prepared from deuteriocarbinol **6d** in 90% yield by a previously described procedure.[2] Again, no loss of deuterium was evidenced by NMR: mp 113–114 °C; NMR ($CDCl_3$) δ 2.36 (br s, C_6H_4-*p*-CH_3), 7.18–7.80 (m, C_6H_5, C_6H_4); mass spectrum (70 eV) *m/e* (rel intensity) 331 (27, M^+); $[\alpha]^{25}{}_{D}$ −54.5° (c 3.9, $CHCl_3$).

Anal. Calcd for $C_{15}H_{12}DF_3O_3S$: C, 54.38; H, 3.65. Found: C, 54.26; H, 3.59.

2,2,2-Trifluoro-1-deuterio-1-phenylethylamine (1d). High-pressure ammonolysis of 500-mg portions of tosylate **2d** was conducted for 4 h at 103 °C and 6 kbar in 1-oz screw-cap polyethylene bottles in a conventional high-pressure apparatus previously described.[14] Ammonical THF solutions were prepared by addition of 10% (volume) water to dry THF saturated at 0 °C with ammonia. Amine **1d** was isolated using an extractive workup and is a colorless liquid: bp 88 °C (22 mm); NMR ($CDCl_3$) δ 1.84 (br s, NH), 7.23–7.41 (m, C_6H_5); IR (neat) 3400 (NH), 3000, 1595, 1500, 1460, 1255, 1170, 1120 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 176 (14, M^+), 137 (5), 108 (65), 107 (100).

Anal. Calcd for $C_8H_7DF_3N$: C, 54.55; H, 4.01; N, 7.95. Found: C, 54.41; H, 3.96; N, 7.91.

Acknowledgment. This work was partially supported by grants from the National Science Foundation and the National Institutes of Health.

Registry No.—**1d,** 62929-95-7; (*R*)-(−)-**2d,** 62929-96-8; **6d,** 62929-97-9; (*R*)-(−)-**6d,** 62961-05-1; 2,2,2-trifluoroacetophenone, 434-45-7.

References and Notes

(1) W. H. Pirkle and J. R. Hauske, *J. Org. Chem.*, **42,** 1839 (1977).
(2) W. E. Pereira, Jr., M. Solomon, and B. Halpern, *Aust. J. Chem.*, **24,** 1103 (1971).
(3) (a) J. Hine and R. G. Ghirardelli, *J. Org. Chem.*, **21,** 1550 (1956); (b) J. Hine and W. H. Brader, *J. Am. Chem. Soc.*, **75,** 3964 (1953).
(4) The reported[2] procedure for preparing **3** involves heating the tosylate and hydrazine hydrate to reflux for 12 h. In our hands, this *heterogeneous* reaction affords substantial quantities of a material tentatively identified as the bis-alkylated hydrazine. Use of a cosolvent to render the mixture *ho-*

mogeneous prevents formation of the bis product. For example, overnight heating of a solution of 33 g of tosylate and 32 g of anhydrous hydrazine in 150 mL of triethylene glycol in a 110 °C bath affords complete conversion of tosylate to hydrazine **3** (^{19}F NMR). Under these conditions, deuterated tosylate **2d** affords hydrazine, retaining 89% of the deuterium.

(5) W. J. Le Nobel, *Prog. Phys. Org. Chem.*, **5**, 207 (1967).

(6) For compounds **1**, **2**, **3**, and **6**, the isotopic shift at 84.6 MHz causes the slightly broadened singlet of the deuterated species to coincide with the upfield line of the doublet arising from the protonated species.

(7) Both water and *dry* ethanol have this effect, presumably as a consequence of solvation-altered basicity and nucleophilicity.

(8) W. H. Pirkle, D. L. Sikkenga, and M. S. Pavlin, *J. Org. Chem.*, **42**, 384 (1977).

(9) H. M. Peters, D. M. Fiegl, and H. S. Mosher, *J. Org. Chem.*, **33**, 4245 (1968).

(10) W. H. Pirkle and S. D. Beare, *J. Am. Chem. Soc.*, **89**, 5485 (1967).

(11) The simultaneous determination of two nonidentical enantiomeric purities for compounds differing only by isotopic substitution illustrates the power of chiral solvating agents for NMR determination of enantiomeric purity and absolute configuration.

(12) (a) W. H. Pirkle and J. R. Hauske, *J. Org. Chem.*, **42**, 1839 (1977); (b) W. H. Pirkle and M. S. Hoekstra, *ibid.*, **39**, 3904 (1974).

(13) W. H. Pirkle and R. W. Anderson, *J. Org. Chem.*, **39**, 3901 (1974).

(14) R. A. Grieger and C. A. Eckert, *J. Am. Chem. Soc.*, **92**, 7149 (1970).

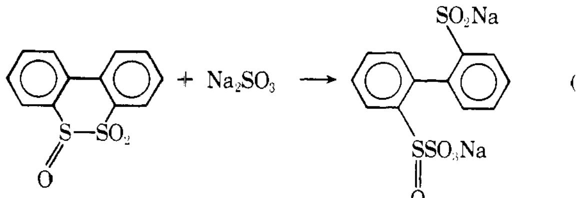
(15) Sodium borodeuteride was purchased from Ventron Corp. and was used without further purification.

Communications

Synthesis and Properties of a Bunte Salt *S*-Oxide[1]

Summary: Reaction of sulfite ion with dibenzo[*c,e*]-1,2-dithiin 1,1,2-trioxide leads to the formation of a compound having a Bunte salt *S*-oxide functional group, $-S(O)SO_3^-$, the first example of a compound with such a functionality; in acid solution the Bunte salt *S*-oxide undergoes a striking and extremely rapid decomposition to the cyclic thiolsulfonate, dibenzo[*c,e*]-1,2-dithiin 1,1-dioxide.

Sir: As part of a general study of the reactions of nucleophiles with oxidized derivatives of dibenzo[*c,e*]-1,2-dithiin we have examined the reaction of sulfite ion with dibenzo[*c,e*]-1,2-dithiin 1,1,2-trioxide[2] (**1**) and have been able to isolate as the exclusive reaction product the salt having structure **2** (eq 1).

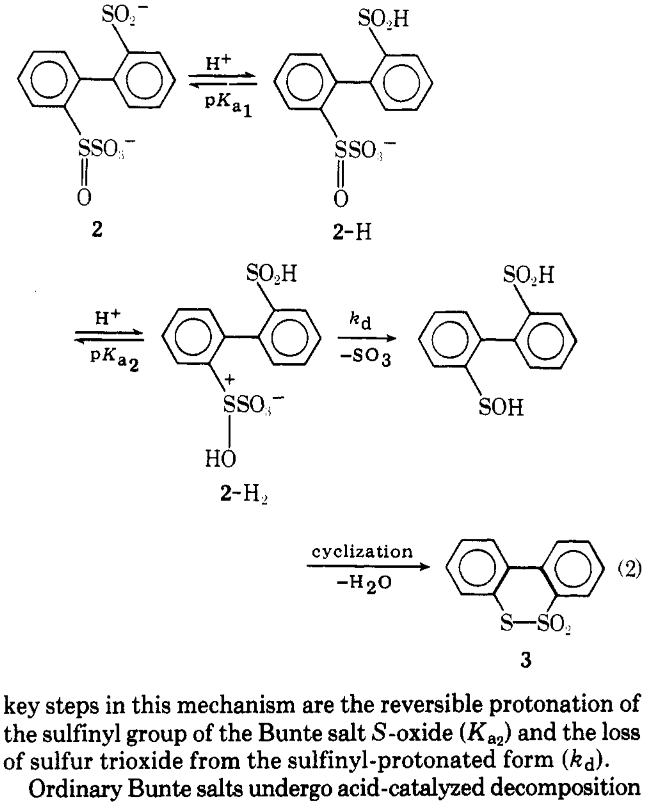


1 2 (1)

Salt **2** contains a Bunte salt *S*-oxide functional group, $-S(O)SO_3^-$, and is the first reported example of a compound containing this functionality. It exhibits some striking and interesting chemical behavior in acid solution.

Bunte salt *S*-oxide **2** was prepared by rapidly adding a 0.05 M solution of **1** in anhydrous dioxane to an equal volume of 0.05 M aqueous sodium sulfite at room temperature. Kinetic studies had shown that the reaction of **1** with sulfite is extremely rapid, $k_2 = 3 \times 10^5$ M^{-1} s^{-1}, and is characterized in the ultraviolet by the disappearance of the absorption maximum at 310 nm characteristic of **1** and the appearance of a new maximum at 280 nm (ϵ 6400) due to **2**. As soon as the addition of **1** to the sulfite solution was complete, the solution was frozen and the solvent was removed by lyophilization to give **2** as a white, powdery solid.[3] The infrared spectrum of **2** (KBr) showed a strong band at 1220 cm^{-1} ($-SO_3^-$) and a series of strong absorptions in the 950–1050-cm^{-1} region (>S=O, $-SO_2^-$, $-SO_3^-$) consistent with structure **2**, but not with any possible isomeric structure.

The stability of **2** in solution and the nature of its decomposition products vary dramatically with the pH of the solution. At 25 °C in 60% dioxane containing 0.01 M HClO$_4$ **2** (10^{-4} M) disappears *extremely rapidly* ($k_1 = 1.2$ s^{-1}) and yields the cyclic thiolsulfonate **3**[4] as the exclusive organic product. In contrast, in a 1:1 acetate/acetic acid buffer **2** disappears much more slowly ($k_1 = 2.2 \times 10^{-4}$ s^{-1}, rate independent of total buffer concentration) and yields *none* of the cyclic thiolsulfonate [the major organic product under these conditions is diphenyl 2,2′-disulfinate[2] (**4**)[5]]. Study of the rate and products of the disappearance of **2** in trifluoroacetate, dichloroacetate, and chloroacetate buffers in 60% dioxane indicates that the facile decomposition of **2** to give thiolsulfonate **3** is acid catalyzed and takes place by the mechanism shown in eq 2. The key steps in this mechanism are the reversible protonation of the sulfinyl group of the Bunte salt *S*-oxide (K_{a_2}) and the loss of sulfur trioxide from the sulfinyl-protonated form (k_d).



Ordinary Bunte salts undergo acid-catalyzed decomposition by an analogous mechanism[6] (eq 3), but at a rate which is