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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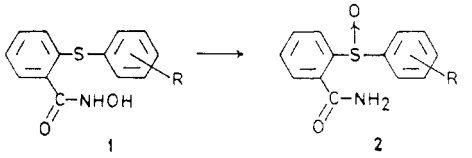
Received March 10, 1986

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]

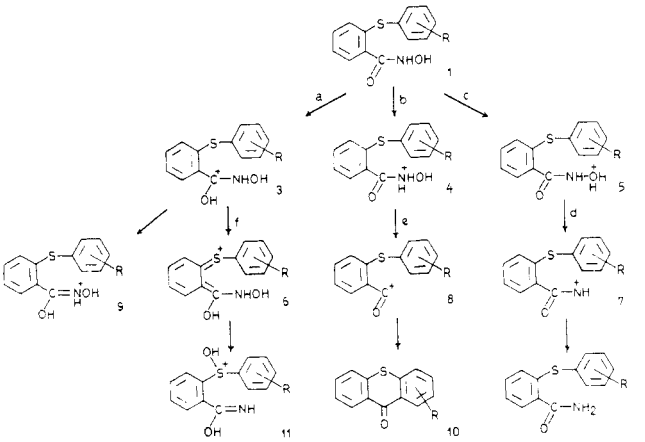


1 2 (1)

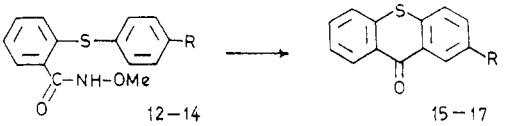
Attempts to monitor the rearrangement of **1** to **2** in deuteriated TFA by using ^1H NMR spectroscopy met with little success. We have been able to observe the emergence of a broad multiplet at δ 8-8.2, presumably the NH signal of the product whose peak area matches with the progress of the reaction.

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).

(1) Usova, E. M.; Koroshin, E. M. *Dokl. Akad. Nauk SSSR* **1957**, *113*, 120; *Chem. Abstr.* **1958**, *52*, 1099a.
(2) Bernadt, D. C.; Fuller, R. L. *J. Org. Chem.* **1966**, *31*, 3312.
(3) Buglass, A. J.; Hudson, K.; Tillet, J. G. *J. Chem. Soc.* **1971**, 123.
(4) Walter, W.; Schaumann, E. *Justus Liebigs Ann Chem.* **1971**, *743*, 154.
(5) Lobo, A. M.; Prabhakar, S.; Fonseca, M. T. C.; Rodriguez, A. M. B. *Tetrahedron Lett.* **1977**, 3167.
(6) Dhareshwar, G. P.; Chhaya, P. N.; Hosangadi, B. D. *Indian J. Chem., Sect. B* **1980**, *19B*, 831.

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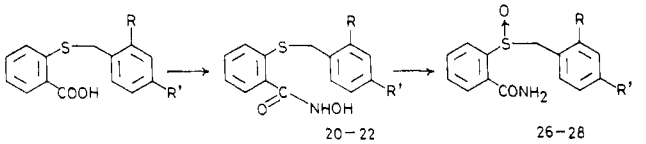
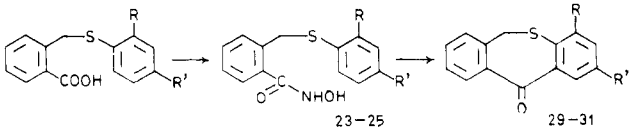
Scheme III



20–22 26–28

	R	R'
20, 23, 26, 29 :	H	H
21, 24, 27, 30 :	H	Me
22, 25, 28, 31 :	OMe	H

Scheme IV

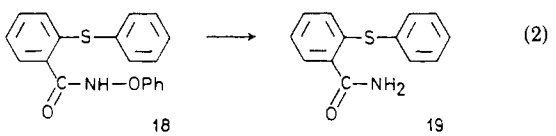


23–25 29–31

Pathway e generates acyl cation **8**, which would cyclize to give thioxanthenone (**10**). We have already reported the formation of **10** when medium of rearrangement is changed from polyphosphoric acid (PPA) to sulfuric acid. This may be attributed to change in acid strength a fact already observed by Lobo and co-workers.[5]

If rearrangement of **1** to **2** were to proceed via **9** or rearranged sulfinium ion **11**, substitution on the hydroxyl oxygen would hardly change the outcome. It should be then possible to generate similar rearrangement in several oxygen-substituted hydroxamic acids.

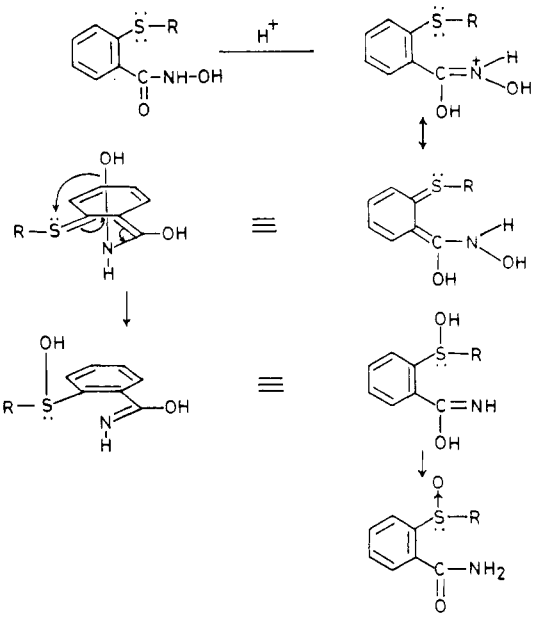
Compounds **12–14** were prepared from corresponding 2-(arylthio)benzohydroxamic acid and *O*-methylhydroxylamine (Scheme II). On treatment with polyphosphoric acid (PPA) at 125 °C for 2 h, compounds **12–17** yielded corresponding thioxanthenones **15–17**. Formation of thioxanthenones **15–17** must have proceeded via acyl cation **8** (Scheme I). In order to facilitate protonation on the hydroxyl oxygen, the corresponding *O*-phenyl-substituted hydroxamic acid **18** was prepared from *O*-phenylhydroxylamine hydrochloride.[7] Under identical conditions **18** afforded 2-(phenylthio)benzamide (**19**, eq 2). Formation of **19** may indicate pathway d, but it seems highly improbable because conversion of **7** to **19** would require presence of a reducing agent. It must be admitted that formation of **19** cannot be explained by any of the pathways shown in Scheme I.



18 19 (2)

These results clearly indicate that substitution on the functional group CONHOH does result in different chemistry. As an adjunct it was thought worthwhile to investigate influence of conjugation (via participation of sulfur) on the fate of the reaction. For this purpose hydroxamic acids **20–25** were prepared by hydroxylaminolylsis of corresponding carboxylic acids (Schemes III and IV). On treatment with polyphosphoric acid (PPA), compounds **20–22** afforded rearranged products **26–28** (Scheme III). Compounds **23–25** on the other hand, on treatment with PPA under identical conditions afforded corresponding dibenzothiepinones **29–31** (Scheme IV). Formation of **29–31** indicates that insertion of a methylene group between the thiophenyl group and the benzohydroxamic acid probably favors formation of protonated species **4**. Insertion of a methylene group between the phenyl group and the thiobenzohydroxamic acid group, however, does not seem to influence the fate of reactions. These observations point to extended conjugation being the determining factor in the rearrangement. Based on these arguments a tentative mechanism involving 1,5-sigmatropic shift of **6** can be suggested (Scheme V).

Scheme V



Conclusions. 2-(Arylthio)benzohydroxamic acids and related systems show diverse reactions which may arise due to different protonated species like **3** and **4**. Species **5** seems highly unlikely for various reasons. It could lead to formation of **19** but only in presence of suitable reducing agent. Thus formation of **19** cannot be rationalized. Though no direct evidence of site of protonation is available, it seems reasonable to assume that change in site of protonation due to substituent effect and other electronic parameters may be responsible for variety pathways as suggested in Scheme I. As an adjunct, rearrangement of **1** to **2** can be rationalized by mechanistic scheme (Scheme V) which involves 1,5-sigmatropic shift.

Experimental Section

Preparation of Hydroxamic Acids 12–14.[8] A mixture of *O*-methylhydroxylamine hydrochloride[10] (0.01 mol), 2-(arylthio)benzoyl chloride (0.01 mol), and dry pyridine (5 mL) was heated on a steam bath for 30 min and then diluted with anhydrous ether. Pyridine hydrochloride which precipitated out was filtered off. The ether extract was washed successively with saturated sodium bicarbonate solution (2 × 50 mL) and sodium hydroxide solution (10%, 2 × 50 mL). Acidification of sodium hydroxide extract gave **12–14** in 58–62% yields.

Preparation of Hydroxamic Acid 18.[8] A mixture of *O*-phenylhydroxylamine hydrochloride[7] (0.01 mol), 2-(phenylthio)benzoyl chloride (0.001 mol), and dry pyridine (5 mL) were heated on a steam bath for 30 min. After the workup as described in preceding procedure, **18** was obtained in 56% yield.

Preparation of Hydroxamic Acids 20–25.[9] A mixture of hydroxylamine (0.01 mol, generated by action of methanolic potassium hydroxide on hydroxylamine hydrochloride), the corresponding carboxylic acid (0.01 mole), and dicyclohexylcarbodiimide (0.01 mol) were stirred at 20 °C for 1 h. Methanol was removed under reduced pressure. The solid mass was ex-

(7) Nicholson, J. S.; Peak, D. A. *Chem. Ind. (London)* **1962**, 1244.

(8) Nimbalkar, M. M. Ph.D. Thesis, University of Bombay, 1983.
(9) Chhaya, P. N. Ph.D. Thesis, University of Bombay, 1982.
(10) Fujii, T.; Wee, C.; Yamada, S. I. *Chem. Pharm Bull.* **1967**, *15*, 345.

tracted with sodium hydroxide solution (10%, 50 mL). Acidification of alkaline layer afforded hydroxamic acids **20–25** in 55–60% yield.

Preparation of Thioxanthenones 15–17.[11] 2-(Arylthio)benzoic acid (0.01 mol) was treated with concentrated sulfuric acid (10 mL) for 1 h at room temperature. Decomposition of reaction mixture in crushed ice gave a sticky residue. It was extracted with benzene. The organic layer after washing with sodium hydroxide solution (10%, 2 × 50 mL) and on evaporation afforded thioxanthenones in 60–65% yield.

Preparation of Dibenzo[*b,e*]thiepin-11(6*H*)-ones 29–31.[9-13] 2-[(Arylthio)methyl]benzoic acid (0.01 mol) was treated with concentrated sulfuric acid (10 mL). After the workup as described earlier, **29–31** were obtained in 60–65% yield.

Preparation of 2-[(Arylmethyl)sulfinyl]benzamides 26–28.[9] 2-[(Arylmethyl)thio]benzoic acid[9] (0.01 mol) was refluxed with phosphorus pentachloride (3.5 g) in dry benzene (30 mL) for 2 h. After the removal of volatile material, the residue was cooled and treated with aqueous ammonia (30%, 15 mL). 2-[(Arylmethyl)thio]benzamide, which precipitated, was filtered off and dissolved in acetone (10 mL). Hydrogen peroxide (10%, 1 mL) was added to it, and the mixture was kept overnight at room temperature. It was then decomposed in cold water to give **26–28** in 55–60% yield.

General Method of Reactions of Hydroxamic Acids in PPA. Hydroxamic acid (1.0 g) was treated with PPA [P_2O_5 (20 g), H_3PO_4 (12 mL)]. The reaction mixture was heated in an oil bath at 120–125 °C for 2 h. After cooling, the reaction mixture was treated with crushed ice and extracted with chloroform (2 × 30 mL). The organic layer was washed successively with saturated sodium bicarbonate solution (2 × 25 mL), sodium hydroxide solution (10%, 2 × 25 mL), and water. The organic layer, on evaporation gave products. In each case the structure of the product was established on basis of spectral data and comparison with authentic sample prepared by standard methods described above.

Preparation of 2-(Phenylthio)benzamide (19).[12] *O*-Phenyl-2-(phenylthio)benzohydroxamic acid **18** (0.5 g, 0.0015 mol) was treated with PPA (10 g of P_2O_5 + 6 g of H_3PO_4) at 125 °C for 2.5 h. After the usual workup as given in the method described above, it afforded a neutral residue. The neutral residue was fractionally crystallized from methanol to give a compound, mp 207 °C, yield 55%. The mother liquors from the above furnished a compound with mp 178 °C.

The compound with mp 207 °C was identified as thioxanthenone (**15**). The compound with mp 178 °C was identical with 2-(phenylthio)benzamide (**19**).

Registry No. **12**, 89114-60-3; **12** (acid chloride), 53732-61-9; **13**, 104351-53-3; **13** (acid chloride), 61485-96-9; **14**, 89114-61-4; **14** (acid chloride), 43183-12-6; **15**, 492-22-8; **16**, 15774-82-0; **17**, 40478-82-8; **18**, 104351-54-4; **19**, 31913-94-7; **20**, 104351-55-5; **20** (acid), 1531-80-2; **21**, 104351-56-6; **21** (acid), 104351-51-1; **22**, 104351-57-7; **22** (acid), 104351-52-2; **23**, 104373-43-5; **23** (acid), 1699-03-2; **24**, 104351-58-8; **24** (acid), 5202-10-8; **25**, 104351-59-9; **25** (acid), 82387-28-8; **26**, 54705-25-8; **26** (thioether), 54705-18-9; **27**, 104351-60-2; **27** (thioether), 104351-62-4; **28**, 104351-61-3; **28** (thioether), 104351-63-5; **29**, 1531-77-7; **30**, 5202-11-9; **31**, 82387-29-9; CH_3OHN_2·HCl, 593-56-6; $C_6H_5ONH_2$·HCl, 6092-80-4.

(11) Szmant, H. H. *J. Org. Chem.* **1953**, *18*, 745.
(12) Dhareshwar, G. P.; Hosangadi, B. D. *Indian J. Chem., Sect. B* **1978**, *16B*, 143.
(13) Gadient, F.; Jucker, E.; Linderman, A.; Treschker, M. *Helv. Chim. Acta* **1962**, *45*, 1860.

Fluorosulfonation. Insertion of Sulfur Trioxide into Allylic C–F Bonds[1,2]

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Received June 25, 1986

Insertion of sulfur trioxide into allylic C–F bonds of both terminal and internal fluoro olefins is shown to form the most stable olefinic products. A mechanism involving fluoroallyl cations as intermediates is proposed. State-of-the-art ab initio calculations of the ground-state energies for two isomeric unsaturated fluoro ethers establish the slightly greater stability (5.7 kcal/mol) of a vinyl ether over the corresponding fluoro olefin. A description of the optimized geometries of these molecules is also presented.

The early literature on reactions of fluoro olefins with sulfur trioxide shows that terminal fluoro olefins normally undergo cycloaddition to form sultones.[3,4] These sultones are readily isolated unless nonfluorinated substituents are present to facilitate further reaction.[5] On the other hand, few instances of detectable cycloadducts with internal fluoro olefins have been reported.[6,7] As is illustrated below, cycloaddition of SO_3 to an internal fluoro olefin bearing no electron-donating substituents is generally so sluggish that insertion into allylic C–F bonds is the pre-

(1) Contribution no. 4133 from E. I. du Pont de Nemours & Company, Central Research & Development Department, Experimental Station, Wilmington, DE 19898.
(2) (a) For a preliminary communication on part of this work, see: Krespan, C. G.; England, D. C. *J. Am. Chem. Soc.* **1981**, *103*, 5598. (b) For details on the early syntheses and reactions of *F*-allyl fluorosulfate, see also: U.S. Pat. 4 206 138, 1980; U.S. Pat. 4 235 804, 1980; U.S. Pat. 4 292 449, 1981.
(3) England, D. C.; Dietrich, M. A.; Lindsey, R. V. *J. Am. Chem. Soc.* **1960**, *82*, 6181.
(4) Knunyants and Sokolski (Knunyants, I. L.; Sokolski, G. A. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 583) review the literature on synthesis and reactions of fluorinated β-sultones.
(5) (a) Krespan, C. G.; Smart, B. E.; Howard, E. G. *J. Am. Chem. Soc.* **1977**, *99*, 1214. (b) Smart, B. E.; Krespan, C. G. *J. Am. Chem. Soc.* **1977**, *99*, 1218.
(6) (a) Several cycloadditions which are tabulated in ref 4 may be in error. As documented here, $CF_3CCl{=}CClCF_3$ was found to undergo allylic insertion only, rather than the cycloaddition ascribed to ref 6b. Studies (ref 8) with SO_3 and $CF_3CCl{=}CCl_2$ also found that C—F insertion is the only reaction to occur with or without catalyst. Furthermore, the several stable sultones obtained from alkyl fluorovinyl ethers as cited in ref 4 are at variance with more recent work (see ref 5a). (b) *Chem. Abstr.* **1958**, *52*, 15493.
(7) Smart (Smart, B. E. *J. Org. Chem.* **1976**, *41*, 2353) reports perhaps the earliest examples of insertion in the special case of SO_3 and polyfluorocyclobutenes. No cycloadducts were detected.

0022-3263/86/1951-4460$01.50/0