Sulfuranes. IX.[1] Sulfuranyl Substituent Parameters. Substituent Effects on the Reactivity of Dialkoxydiarylsulfuranes in the Dehydration of Alcohols[2]

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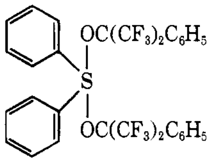
Abstract: We report the synthesis and characterization of four substituted analogs of sulfurane $(C_6H_5)_2S(OR_F)_2$ (where $R_F = C_6H_5C(CF_3)_2$), with *S*-phenyl substituents 3-fluoro, 4-fluoro, 4,4′-di-*tert*-butyl, and 4,4′-dimethoxy. Competitively determined relative rate constants for the reactions of *tert*-butyl alcohol with these sulfuranes in chloroform at −41° were correlated with σ values, with $\rho = -1.68$. The implications with respect to the mechanism of alcohol dehydration with sulfuranes are discussed. These sulfuranes are converted by treatment with trifluoromethanesulfonic acid to crystalline, salt-like diarylalkoxysulfonium triflates. Inductive and resonance parameters (σ_I, σ_R) are determined for the phenylthio (0.21, −0.08), phenylsulfinyl (0.51, −0.01), phenylsulfonyl (0.52, 0.14), phenyldialkoxysulfuranyl (0.40, 0.09), and phenylalkoxysulfonium (1.31, 0.31) substituents, using the ^{19}F nmr chemical shift correlation of Taft. The values of σ_I and σ_R for the sulfuranyl substituent are discussed in terms of hypervalent bonding models.

The isolation,[3] characterization,[3] chemical behavior,[1,4] and X-ray structure[5] of dialkoxydiarylsulfurane (1) have recently been reported. The surprising stability and promising synthetic utility of this first example of a ketal analog of a sulfoxide are of considerable theoretical interest. The present work uses substituent effects to delineate electronic interactions in **1** and its analogs, and to study the mechanism of their reaction with *tert*-butyl alcohol.



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Experimental Section

m-**Fluorophenyl Phenyl Sulfide.** This compound was prepared by a method analogous to that reported for the para isomer.[6] Potassium thiophenoxide (13 g, 0.089 mol) and 25 g (0.111 mol) of *m*-fluoroidobenzene were heated at 235–240° for 6 hr. The reaction mixture was treated with 35 ml of ethanol and acidified with 5% H_2SO_4, and zinc dust was added. The mixture was steam distilled and the zinc cake extracted with ten 15-ml portions of ether; the ether extracts were combined and dried ($MgSO_4$), and the solvent was removed. The resulting yellow oil was fractionally distilled twice, bp 112–113° (2.0 mm), to give 7.0 g (40%) of the sulfide. *Anal.* Calcd for $C_{12}H_9FS$: C, 70.56; H, 4.44; S, 15.69. Found: C, 70.39; H, 4.25; S, 15.85.

p-**Fluorophenyl Phenyl Sulfide.** The method described for the meta isomer gave material with bp 133–135° (8 mm), lit.[6] bp 141–142° (11 mm).

m-**Fluorophenyl Phenyl Sulfoxide.** This compound was prepared by basic hydrolysis of the corresponding sulfurane, **2b**. A solution containing 1 g (0.0014 mol) of **2b** in 10 ml of ether was extracted four times with 10% potassium hydroxide, the ether was dried ($MgSO_4$), and the solvent was removed. The white powder was twice recrystallized from ether–pentane giving transparent crystals, mp 62–63°, 0.28 g (91%). *Anal.* Calcd for $C_{12}H_9FOS$: C, 65.45; H, 4.08. Found: 65.16; H, 4.17.

p-**Fluorophenyl Phenyl Sulfoxide.** Basic hydrolysis of **2a** leaves a clear oil, lit.[7] bp 148–149° (3 mm): mass spectrum (70 ev), *m/e* (rel intensity) 220 (100), 172 (59), 109 (71), 77 (53); ir (neat), 1040 cm^{-1} (S=O).

m-**Fluorophenyl Phenyl Sulfone.** An ice-cold solution of *m*-fluorophenyl phenyl sulfide, 0.5 g (0.0024 mol), in 5 ml of carbon tetrachloride was treated with a carbon tetrachloride solution containing 0.82 g (0.005 mol) of ruthenium tetroxide.[8] The precipitated ruthenium dioxide was filtered and washed with five 10-ml portions of chloroform. The filtrate and the washes were combined, and the solvent was removed. The white solid was recrystallized twice from chloroform–pentane to give pure sulfone, mp 96–97°, 0.45 g (80%). *Anal.* Calcd for $C_{12}H_9FO_2S$: C, 61.00; H, 3.84; S, 13.57. Found: C, 61.16; H, 3.89; S, 13.58.

p-**Fluorophenyl Phenyl Sulfone.** Ruthenium tetroxide oxidation of *p*-fluorophenyl phenyl sulfide, using the above procedure, gave 0.42 g (75%) of the sulfone, mp 111–112° (lit.[6] 109.5–110°).

General Synthesis for Dialkoxydiarylsulfuranes. Hexafluoro-2-phenyl-2-propanol[9] (R_FOH) was purified and dried by fractional distillation from P_2O_5. The potassium alkoxide was prepared by the addition of potassium metal (71.7 g, 1.81 g-atoms) to a solution of R_FOH (334.4, 1.37 mol) in 2 l. of ether (dried over sodium wire) contained in a specially designed reaction vessel with a sintered-glass bottom and equipped with a Dry Ice–acetone condenser. A stream of dry nitrogen was directed upward through the filter. After 24-hr the alkoxide solution was filtered into a receiving flask and its concentration determined by nmr. This was used as a stock alkoxide solution for all the syntheses.

In a flask equipped with a Dry Ice–acetone condenser, gas inlet tube, and magnetic stirrer (all of which were assembled hot after oven drying) was placed 1 equiv of the appropriate diaryl sulfide, 2 equiv of KOR_F, and enough dry ether to dissolve everything. A jacket was placed around the reaction flask and filled with powdered Dry Ice. Throughout the reaction a gentle stream of dry nitrogen was directed through the gas inlet tube. One equivalent of chlorine (dried by passage through a P_2O_5 column) was condensed into a calibrated trap and then swept into the reaction mixture with dry nitrogen. After 1 hr at −78° the reaction mixture was allowed to warm to room temperature. (In a variant of the synthesis, used for **1** only, the entire reaction was run at room temperature. Yields were not appreciably affected.) The precipitated KCl was filtered in a nitrogen-atmosphere drybox and the solvent removed from the

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(1) For paper XIII in this series, see E. F. Perozzi and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 5519 (1972).

(2) Abstracted from the B.S. thesis of L. J. K., University of Illinois, Urbana, Ill., 1972.

(3) R. J. Arhart and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 4997 (1972); J. C. Martin and R. J. Arhart, *ibid.*, **93**, 2339, 2341 (1971).

(4) R. J. Arhart and J. C. Martin, *ibid.*, **94**, 5003 (1972); J. C. Martin and R. J. Arhart, *ibid.*, **93**, 4327 (1971).

(5) I. C. Paul, J. C. Martin, and E. F. Perozzi, *ibid.*, **94**, 5010 (1972); *ibid.*, **93**, 6674 (1971).

(6) N. J. Leonard and L. E. Sutton, *ibid.*, **70**, 1564 (1948).

(7) R. J. Maner, Ph.D. Thesis, University of Iowa, 1968.

(8) C. Djerassi and R. R. Engle, *J. Amer. Chem. Soc.*, **75**, 3838 (1953).

(9) B. S. Farah, E. E. Gilbert, and J. P. Siblia, *J. Org. Chem.*, **30**, 998 (1965).

filtrate *in vacuo.* Products varied in form from white crystals to a yellow oil. Purification of crystalline products was accomplished by recrystallization from ether–pentane mixtures. The oils were purified by washing with cold pentane and removal of volatile materials under high vacuum ($<10^{-4}$ mm). This resulted in the formation of crystals, which were recrystallized from ether–pentane.

***m*-Fluorophenylsulfurane (2b).** A solution of *m*-fluorophenyl phenyl sulfide, (4.30 g, 0.021 mol), when treated by the general method, gave crude sulfurane as a yellow powder, which was recrystallized to give **2b**: mp 98–100° (sealed tube), 8.2 g (57%); 220 MHz ^{1}H nmr (CDCl$_3$), δ 7.9 (m, 1, proton ortho to S and F of SC$_6$H$_4$F), 7.7 (m, 2), 7.3 (m, 16); ^{19}F nmr (ether, −48°), 68.1 ppm (s, C*F*$_3$), 73.4 (s, small R$_F$OH impurity resulting from hydrolysis of **2b**); mass spectrum, *m/e* 690 (M$^+$), 447 (M$^+$ − OR$_F$), high resolution peak matching, *m/e* 690.0938 (calcd for **2a**; 690.0898). *Anal.* Calcd for $C_{30}H_{19}O_2F_{13}S$: C, 52.18; H, 2.77; S, 4.64. Found: C, 52.34; H, 2.95; S, 4.40.

***p*-Fluorophenylsulfurane (2a).** *p*-Fluorophenyl phenyl sulfide (5.86 g, 0.028 mol) gave crude sulfurane as a white powder, which was recrystallized to give pure **2a**: mp 128–131° (sealed tube); 15.2 g (80%); 220-MHz ^{1}H nmr (CDCl$_3$) δ 7.9 (m, 2, aromatic CH, ortho to S), 7.6 (m, 2), 7.2 (m, 15): ^{11}F nmr (ether, −48°) 68.1 ppm (s, CF$_3$), 73.4 (s, small impurity resulting from hydrolysis of **2a**); mass spectrum, *m/e* 690 (M$^+$), 447 (M$^+$ − OR$_F$), high resolution peak matching *m/e* 690.0887 (calcd for **2a**; 690.0898). *Anal.* Calcd for $C_{30}H_{19}O_2F_{13}S$: C, 52.18; H, 2.77; S, 4.64. Found: C, 51.62; H, 2.92; S, 4.57.

Bis(*p-tert*-butylphenyl)sulfurane (2c). A solution of bis(*p-tert*-butylphenyl) sulfide[10] (40 g, 0.134 mol) gave a yellow oil, which was purified by the general method to give **2c**: mp 138.5–140° (sealed tube); 45 g (42%); 220-MHz ^{1}H nmr (CDCl$_3$) δ 7.9 (d, 4, J = 9 Hz, ortho protons, S-aryl), 7.4 (m, 8, aromatic CH, meta to S, and ortho protons of OR$_F$), 7.2 (m, 6, meta and para aromatic CH of OR$_F$), 1.4 (s, 18, CH$_3$); ^{11}F nmr (ether, −48°) 68.3 ppm (s, CF$_3$), 73.4 (s, small impurity resulting from hydrolysis of **2c**); mass spectrum, *m/e* 784 (M$^+$), 541 (M$^+$ − OR$_F$), and 540 (M$^+$ − HOR$_F$), high resolution peak matching *m/e* 784.2232 (calcd for **2c**, 784.2244). *Anal.* Calcd for $C_{38}H_{36}O_2SF_{12}$: C, 58.19; H, 4.59; S, 4.09. Found: C, 58.07; H, 4.89; S, 3.95.

Bis(*p*-methoxyphenyl)sulfurane (2d). 4,4′-Dimethoxydiphenyl sulfide[7] (23 g, 0.93 mol) was treated by the standard procedure. The work-up procedure was modified, because sulfurane **2d** precipitated from the ether solution. The total precipitate was filtered and extracted with ten 50-ml portions of chloroform. The white crystals obtained upon removal of solvent were purified by washing with cold ether to give pure **2d**: mp 138–139°, 10 g (15%); 220-MHz ^{1}H nmr (CDCl$_3$) δ 7.8 (d, 4, J = 9 Hz, aromatic CH, ortho to S), 7.4 (m, 4, ortho aromatic CH of OR$_F$), 7.2 (m, 6, meta and para aromatic CH of OR$_F$), 6.9 (d, 4, J = 9 Hz, aromatic CH meta to S), 3.8 (s, 6, OCH$_3$); ^{19}F nmr (CDCl$_3$, 41°) 70.4 ppm (s, CF$_3$); mass spectrum, *m*/e 732 (M$^+$), 509 (M$^+$ − OR$_F$), 508 (M$^+$ − HOR$_F$). *Anal.* Calcd for $C_{32}H_{24}O_4F_{12}S$: C, 52.46; H, 3.30; S, 4.37. Found: C, 51.98; H, 3.30; S, 4.14.

Triflate 3a. To an ice-cold solution of sulfurane **2a** (0.51 g, 0.73 mmol) in 2 ml of ether cooled to −78° was added 65 μl (0.72 mmol) of trifluoromethanesulfonic acid. The triflate, which precipitated immediately as a white powder, was purified by washing several times with ether to give pure **3a**, 0.36 g (83%): ^{1}H nmr (CDCl$_3$) δ 8.2 (m, 4, aromatic CH ortho to S), 7.6 (m, 10); ^{19}F nmr (CDCl$_3$, 41°) 69.7 ppm (m, 6, OC(CF$_3$)$_2$), 79.0 (s, 3, SCF$_3$). *Anal.* Calcd for $C_{22}H_{14}O_4F_{10}S_2$: C, 44.23; H, 2.53; S, 10.73. Found: C, 44.04; H, 2.74; S, 10.64.

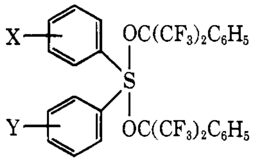
Triflate 3b. To a solution of **2b,** 0.46 g (0.67 mmol) in 4 ml of ether, was added 59 μl (0.67 mmol) of trifluoromethanesulfonic acid to give 0.30 g (74%) of triflate **3b**. This was purified as was **3a**. ^{1}H nmr (CDCl$_3$) δ 8.1 (m, 4, aromatic CH ortho to S), δ 7.5 (m, 10); ^{19}F nmr (CDCl$_3$) 69.7 ppm (m, 6, OC(CF$_3$)$_3$), 79.0 (s, 3, SCF$_3$). *Anal.* Calcd for $C_{22}H_{14}O_4F_{10}S_2$: C, 44.23; H, 2.53; S, 10.73. Found: C, 43.99; H, 2.58; S, 10.71.

Calibration of ^{19}F Spectra. The ^{19}F chemical shifts were calibrated by a method similar to that described by Taft, *et al.*[11] Proton-decoupled spectra were obtained on a Varian HA-100 spectrometer at 94.1 MHz using a 7% solution of fluorobenzene for an internal lock and chemical shift standard. The solvent was carbon tetrachloride for all compounds except the triflate salts, **3a** and **3b**, for which we used chloroform. The chemical shifts of the fluorobenzene could be measured with an accuracy of ±0.1 Hz. In most cases measurements were made at three dilutions (*ca.* 20, 10, and 5%) and chemical shifts obtained by extrapolation to infinite dilution. Typical extrapolations were on the order of 5 Hz.

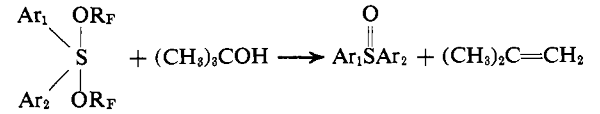
Competitive Kinetics. A chloroform solution of approximately 1 equiv of each of two sulfuranes was placed in a constant-temperature bath at −41°. *tert*-Butyl alcohol, 1.5 equiv, was slowly distilled *in vacuo* into the stirred sulfurane solution. After the addition of the alcohol was complete (*ca.* 1 hr), hydroquinone sufficient to reduce the remaining 0.5 equiv of sulfurane was added in tetrahydrofuran solution. The resultant mixture containing diaryl sulfides, diaryl sulfoxides, and benzoquinone was analyzed by glpc on a 0.25 in. × 2 ft column, 20% SE-30 on Chromosorb W, DCMS. Relative concentrations were determined from peak areas by comparison with known mixtures.

Results

Synthetic. The synthesis of dialkoxydiarylsulfuranes reported earlier,[3] which involved the treatment of an ether solution of diaryl sulfide and 2 mol of potassium alkoxide with 1 equiv of chlorine at −78°, was found to proceed in equally high yield at room temperature. Sulfuranes **2a–d**, substituted analogs of the previously reported sulfurane **1**, were prepared. Sulfuranes **2a–d** show chemical behavior very similar to that reported for **1**. These extremely hygroscopic compounds all hydrolyze rapidly in the air to give 1 mol of diaryl sulfoxide and 2 mol of R$_F$OH. All dehydrate *tert*-butyl alcohol rapidly to form isobutylene.



2a, X = *p*-F; Y = H
b, X = *m*-F; Y = H
c, X = Y = *p*-*t*-Bu
d, X = Y = *p*-OCH$_3$



The mass spectra of sulfuranes **2a–d** all show weak molecular ions (*ca.* 2% of the base peak at 70 eV). A prominent fragment present in all spectra corresponds to a loss of one alkoxy ligand to give an alkoxysulfonium ion. The more reactive sulfuranes, **2c–d**, also show a prominent peak corresponding to the loss of an R$_F$OH group. This could result from a pyrolysis similar to that reported[3] for **1**, to give alkoxyaryl aryl sulfide and R$_F$OH in the mass spectrometer inlet. Sulfuranes **2c,d** also give a significant M − 2 peak. Further work will be required to establish the origin of this peak.

The trifluoromethanesulfonate (triflate) analogs of **2a** and **2b** were prepared by reaction with trifluoromethanesulfonic acid. Solutions of **2a** and **2b** in ether gave precipitates of the salt-like triflates, **3a** and **3b**.

Substituent Parameters from ^{19}F Chemical Shifts. Taft's equations, (1) and (2), relate ^{19}F chemical shifts in para- and meta-substituted fluorobenzenes to the inductive substituent constant, σ_I, and the resonance substituent constant, σ_R, of the substituent.[11] Chem-

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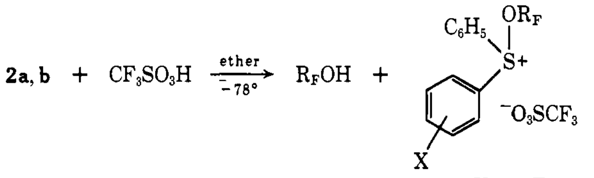
(10) V. Franzen, H. J. Schmidt, and C. Mertz, *Chem. Ber.*, **94**, 2942 (1961).

(11) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709, 3146 (1963), and earlier papers.



3a, X = *p*-F
b, X = *m*-F

$$\int_{\mathrm{H}}^{m\text{-}\mathrm{X}} = -7.10\sigma_{\mathrm{I}} + 0.60 \qquad (1)$$

$$\int_{m\text{-}\mathrm{X}}^{p\text{-}\mathrm{X}} = -29.5\sigma_{\mathrm{R}} \qquad (2)$$

ical shifts appropriate for use in these equations are those for infinitely dilute solutions in carbon tetrachloride. The first four entries in Table I are for carbon tetrachloride solutions. Solubility considerations dictated the use of chloroform for the alkoxysulfonium triflate, the final entry in Table I.

Table I. ^{19}F Chemical Shifts[a] for Aryl Sulfur-Substituted Fluorobenzenes

Substituent	Solvent	$\int_{\mathrm{H}}^{m\text{-}\mathrm{X}}$	$\int_{\mathrm{H}}^{p\text{-}\mathrm{X}}$	$\int_{m\text{-}\mathrm{X}}^{p\text{-}\mathrm{X}}$
SC_6H_5	CCl_4	−0.88	+1.40	2.28
SOC_6H_5	CCl_4	−3.05	−3.34	−0.29
$SO_2C_6H_5$	CCl_4	−3.14	−7.23	−4.09
$S(OR_F)_2C_6H_5$	CCl_4	−2.25	−4.86	−2.61
$S^+(OR_F)(C_6H_5)$[b]	$CHCl_3$	−8.71	−18.06	−9.35

[a] In parts per million, extrapolated to infinite dilution. The symbol $\int_{\mathrm{A}}^{\mathrm{B}}$ represents the chemical shift difference for the fluorobenzene substituted with A and with B, following Taft.[11] [b] As the trifluoromethanesulfonate.

Chemical Shifts of CF$_3$ Groups in Mixtures of Sulfuranes. Chemical shift differences (Table II) in the trifluoromethyl groups of the alkoxy ligands of sulfuranes **2a–c** were resolved at 220 MHz.[12] The unsymmetrical diarylsulfuranes, **2a** and **2b**, show nonequivalent CF$_3$ groups, with four-bond F,F coupling giving unresolved quartet structure to the two peaks of a single sulfurane, as expected[3] for prochiral sulfuranes of this type. At 56 MHz only a single peak was seen for each of these sulfuranes.

Table II. ^{19}F Chemical Shifts for Trifluoromethyl Groups of Sulfuranes **2a–c**[a]

Sulfurane	$\Delta\delta$[a]	Multiplicity
2a	0.114	q, $J \simeq 10$ Hz
	−0.73	q, $J \simeq 10$ Hz
2b	0.145	q, $J \simeq 10$ Hz
	−0.086	q, $J \simeq 10$ Hz
2c	0.052	s

[a] Chemical shifts in ppm relative to internal standard unsubstituted sulfurane **1** in CDCl$_3$ at 28°.

A solution of equimolar amounts of **1** and the *m*-fluorophenylsulfurane (**2b**) in chloroform-*d* gave a well-resolved spectrum in the CF$_3$ region at 28°. Upon additions of increments of R$_F$OH peak broadening, resulting from ligand exchange with R$_F$OH, was more noticeable for **1** than for **2b**. After addition of sufficient R$_F$OH (*ca.* 0.002 *M*) to bring about coalescence of the peak for **1** with that for R$_F$OH ($\Delta\delta$, *ca.* 1200 Hz) the ligand exchange with **2b** was proceeding only rapidly enough to coalesce the two nonequivalent CF$_3$ groups of **2b** ($\Delta\delta$, *ca.* 85 Hz). We can thus estimate that ligand exchange is roughly an order of magnitude more rapid for **1** than it is for **2b**. This suggests a negative value of ρ of appreciable magnitude (*ca.* −3) for the degenerate ligand exchange reaction.

Competitive Kinetics. The relative reactivities of sulfuranes **1** and **2a–d** toward *tert*-butyl alcohol were determined using the integrated rate equation, (3).

$$k_{\mathrm{rel}} = \frac{\log[(A - X)/A]}{\log[(B - Y)/B]} \qquad (3)$$

This equation requires that the amount of starting material, A and B, present initially, and the amount of starting material remaining after reaction, $(A - X)$ and $(B - Y)$, be known. In these experiments these quantities were determined indirectly by the following scheme, using glpc to determine relative amounts of sulfide and sulfoxide. The mixture of sulfides and sulfoxides was analyzed by glpc. Initially the experiment was carried out by direct addition of a dilute solution of *tert*-butyl alcohol, with swirling, into the cooled solution of sulfuranes. Under these conditions stirring control of relative reaction rates was observed. The more reactive sulfuranes **2c** and **2d** reacted nearly statistically while **2a** and **2b** showed some partitioning between substituent effects and stirring control. The rates of dehydration are very rapid even at −41°. Satisfactory relative rates (Table III) were obtained when the dehydration was carried out by slow bulb-to-bulb distillation of the *tert*-butyl alcohol, *in vacuo*, into a rapidly stirred solution of sulfuranes at −41°. The reduction of sulfuranes to sulfides with hydroquinone

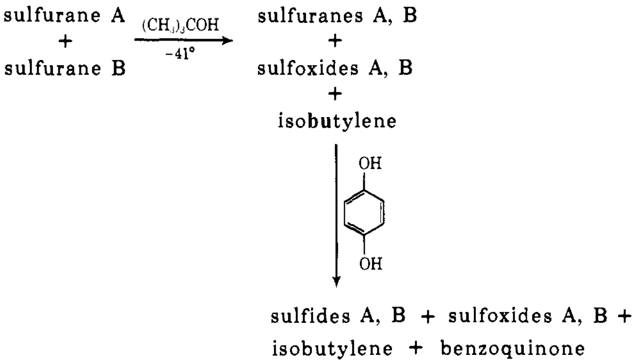


Table III. Relative Rates of Dehydration of *tert*-Butyl Alcohol by Sulfuranes at −41°

Sulfurane	k_{rel}	Log k_{rel}	$\Sigma\sigma$[a]
1	1.0	0	0
2a	0.87	−0.06	0.06
2b	0.36	−0.44	0.34
2c	5.74	0.76	−0.40
2d	9.97	1.00	−0.54

[a] Values of σ based on the ionization of benzoic acids, from D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

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(12) We are grateful to Mr. Robert Thrift for determining the conditions necessary to attain the requisite 54.9-kG field for 220-MHz ^{19}F spectra, using a Varian 220-MHz nmr spectrometer.

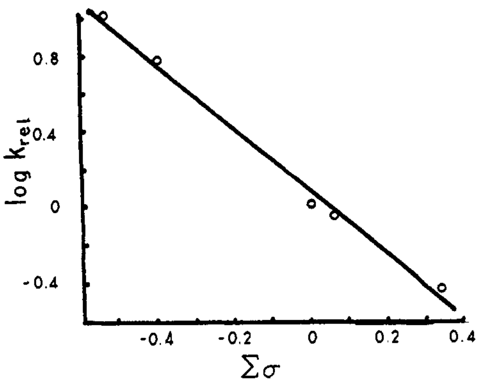

Figure 1. Hammett plot for the dehydration of *tert*-butyl alcohol by sulfuranes **1** and **2a–d** at −41° in chloroform.

was shown to be essentially quantitative. With suitable care to exclude moisture less than 1% of sulfoxide product is formed.

A plot of the data in Table III gives an excellent Hammett correlation with σ values (Figure 1), $\rho = -1.68 \pm 0.08$ (the uncertainty expressed is the standard deviation). The correlation with σ^+ is greatly inferior.

Discussion

Substituent Parameters. In an earlier paper of this series[5] the X-ray crystal structure of sulfurane **1** was reported. The trigonal-bipyramidal geometry of **1** is consistent[5] with a bonding scheme analogous to that advanced by Rundle[13] to describe the bonding in xenon difluoride. Similar schemes have been proposed for various other hypervalent species, including those of sulfur.[14] In this picture the sulfur p_z orbital and one p orbital from each of the oxygens are used in a delocalized three-centered four-electron bonding scheme. Two of the electrons occupy the bonding MO, distributed over all three atoms, and two are in the nonbonding orbital with electron density on the apical oxygens. In this oversimplified picture the apical oxygens incur net formal negative charge and the sulfur net formal positive charge (in the zero-order approximation, two-thirds unit positive charge). Taft's correlation of ^{19}F chemical shifts of substituted fluorobenzenes with substituent parameters has provided an excellent probe for electronic effects related to the charge distribution on this hypervalent substituent group. Table IV provides the basis for comparison between the sulfuranyl substituent and substituents with the more usual oxidation and charge states of sulfur (sulfide, sulfoxide, sulfone, and sulfonium). Values from this work for substituent parameters for the *S*-phenyl members of this series agree closely with literature values for their *S*-methyl analogs[11] and for the one case (phenylthio) for which a literature value[15b] is available.

All of the inductive constants, σ_I, listed in Table IV are positive, reflecting substituent electron withdrawal by induction. The magnitude of the σ_I parameter should be more or less directly related to the amount of positive charge on the central sulfur atom. The inductive effect of the phenyldialkoxysulfuranyl group (σ_I = 0.40) is seen to lie between that of the phenylthio group (0.21) and that of the phenylsulfinyl group (0.51). The much larger value (1.31) of the inductive constant for the alkoxysulfonium cation, which has unit formal positive charge on sulfur, suggests that the charge on the sulfuranyl sulfur is small. In terms of the three-center four-electron bonding picture mentioned above, which ignores possible participation of sulfur 3d orbitals, one might have expected a larger value of σ_I for the sulfuranyl substituent. This result may reflect the importance of d-orbital participation in determining charge distribution.

Table IV. Substituent Parameters for Sulfur- and Phosphorus-Substituted Fluorobenzenes

Substituent	σ_I	σ_R
$S(OR_F)_2C_6H_5$[a]	0.40	0.09
SC_6H_5[a]	0.21 (0.20)[i]	−0.08 (−0.07)[i]
SOC_6H_5[a]	0.51	−0.01
$SO_2C_6H_5$[a]	0.52	0.14
$S^+(OR_F)(C_6H_5)$[b]	1.31	0.31
SCH_3[c]	0.14	−0.17
$SOCH_3$[c]	0.49	0.00
SO_2CH_3[c]	0.55	0.14
SF_3[d]	0.60	0.20
$C_2H_5OP(C_6H_4F)_2(OC_2H_5)$[e]	0.15	0.06
$P(C_6H_4F)_2$[f,g]	0.26	−0.01
$PO(C_6H_4F)_2$[f,h]	0.45	0.12
PF_4[i]	0.45	0.35

[a] This work (in CCl_4). [b] This work (trifluoromethanesulfonate in $CHCl_3$). [c] References 11 (in "normal" solvents). [d] Reference 15. [e] In CH_2Cl_2: B. C. Chung, D. Z. Denney, and D. B. Denney, *J. Org. Chem.*, **36**, 998 (1971). [f] A. W. Johnson and H. L. Jones, *J. Amer. Chem. Soc.*, **90**, 5232 (1968). [g] In C_6H_{12}. [h] In CCl_4. [i] Value in parentheses from Dr. R. G. Pews, quoted in ref 15b. [j] J. W. Rakshys, R. W. Taft, and W. A. Sheppard, *J. Amer. Chem. Soc.*, **90**, 5236 (1968).

The larger value of the only other σ_I substituent constant reported[15] for a sulfuranyl group, that for the SF_3 substituent (+0.60), reflects the greater electronegativity of the fluorine ligands on sulfur. This is also seen in the appreciably more positive σ_R value for the SF_3 group (0.20) than for the alkoxysulfuranyl analog (0.09).

One explanation which might be considered for this low effective electronegativity of the sulfuranyl substituent is related to arguments advanced earlier[5] in a discussion of the distorted trigonal bipyramidal geometry about sulfur in **1**.

4

The ideal trigonal-bipyramidal geometry, with an equatorial C–S–C angle (θ) of 120°, using sp^2 bonds from sulfur, is not seen in members of this series. The expected[16] higher s character for the lone-pair electrons on sulfur, and increased p character in the S–C bonds, is reflected in the C–S–C angle for **1** (**4**, X = OR_F, θ = 104.4°), for the chlorine adduct of a diaryl sulfide (**4**, X = Cl, θ = 108.6°) and for a diaryl sulfide (**4**, X =

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(13) R. E. Rundle, *Surv. Progr. Chem.*, 1, 81 (1963).

(14) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969); J. I. Musher in "Trends in Sulfur Research," T. Wiewiorowski and D. J. Miller, Ed., American Chemical Society, Washington, D. C., 1972, in press.

(15) (a) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, p 353; (b) W. A. Sheppard and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 1919 (1972).

(16) See, for example, H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

no substituent, $\theta = 109.5°$). The decrease in θ with increasing electronegativity of X has been ascribed[5] to the greater preference of the lone pair for s character as the sulfur 3s–3p energy level separation increases with increasing effective nuclear charge on sulfur. Thus, the more positive charge on sulfur the more sulfur p character in the S–C bond. This increase in sulfur p character, shifting electron density toward carbon away from sulfur, tends to decrease the effective electronegativity of the sulfur relative to carbon[18] and partially counteracts the effect of increased charge on sulfur. Results of Denny, quoted in Table IV, for a hypervalent phosphorus analog, suggest that this explanation for the low value of σ_I for the sulfuranyl substituent of **1** is probably not the correct one. The phosphorane of Table IV has three equivalent sp^2 bonds in the equatorial plane with the ideal 120° bond angles. The smaller σ_I seen for the dialkoxyphosphoranyl substituent (0.15) than for the phosphine analog (0.26) is therefore not explicable by invoking increased p character in the P–C bond.

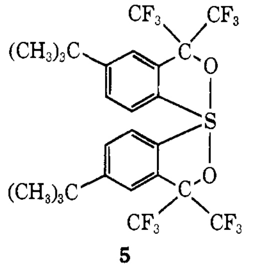
The use of sulfur 3d orbitals in σ- or π-bonding with apical ligands of **1** would increase the electron density on sulfur and result in a decrease in the value of σ_I for the sulfuranyl substituent. Several recent theoretical treatments[17] have suggested that d-orbital participation, in hypervalent bonding of the sort operative in these compounds, contributes relatively little to total bonding energy but may influence charge polarization. It is likely that such d-orbital participation in the bonding of the apical alkoxy ligands of **1** is important in decreasing the positive charge on sulfur. (Central atom 4s orbitals are also judged[17d] unlikely to make energetically important contributions to the bonding of sulfuranes.)

The resonance interaction with electron-donor phenyl ligands in the equatorial plane of **1** is reflected in the σ_R value (0.09), more positive than for the sulfide (−0.08) or the sulfoxide (−0.01) in which the phenyl group accepts electrons by resonance, but less positive than for the strongly electron-withdrawing sulfonyl group (0.14). This order is not the same as the order of σ_I values. The comparison of the sulfurane and the sulfoxide, for example, shows the sulfinyl substituent to be more electron withdrawing by induction, while the sulfuranyl substituent is more electron withdrawing by resonance. The order does not, therefore, appear simply to reflect the increased importance of $p\pi$–$d\pi$ bonding as increased effective positive charge on sulfur, with attendant contraction of d-orbitals,[18] enhances the conjugative interaction. The electron-acceptor interaction of the sulfuranyl substituent with the equatorial phenyl can involve either this $p\pi$–$d\pi$ bonding or interactions with unfilled σ skeletal orbitals of the sulfuranyl group. It has been suggested,[17c] on the basis of extended Hückel calculations, that interactions of the second sort are more important in simple phosphoranes, derivatives of PH_5.

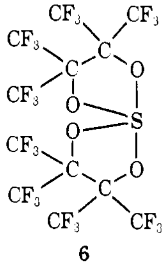
Hoffmann, Howell, and Muetterties[17c] have also discussed experimental and theoretical evidence for a favored conformation for an equatorial π-donor substituent which places the axis of the substituent donor p orbitals in the equatorial plane of a phosphorane. The values of σ_R are very similar for the sulfuranyl and the phosphoranyl substituents listed in Table IV.

No convincing evidence can be presented for the electronically preferred geometry of sulfurane **1**. In the crystal[5] its structure has the two equatorial phenyl rings twisted 33.4 and 42.5° from the equatorial plane. It is obvious that steric interactions strongly disfavor geometries with these rings either in the equatorial plane or perpendicular to it. It is difficult to determine whether the geometry seen for **1**, slightly nearer to the coplanar than to the perpendicular extreme, is more correctly rationalized on the basis of electronic or of steric effects.

Spirosulfurane **5**, in which the phenyl ligands are constrained to the perpendicular geometry, has been reported[19] to differ markedly from **1** in reactivity. It will be of interest to evaluate the importance of steric inhibition or enhancement of resonance of the equatorial π donor type in **5**. The reported unreactivity of **6** toward hydrolysis[20] suggests that the spiro geometry involving bidentate ligands on sulfur is likely to lead generally to a lowering of reactivity.



5



6

Dehydration of Alcohols. The rapid formation of olefins upon treatment of tertiary or secondary alcohols with sulfurane **1** has been shown to be a synthetically useful reaction.[4] The reaction is very rapid for tertiary alcohols. Even at −50° the formation of isobutylene from *tert*-butyl alcohol is complete before an nmr spectrum of the reaction mixture can be obtained. The competitive rate studies used to investigate the mechanism of this reaction failed when solutions of *tert*-butyl alcohol were added dropwise to a solution of a mixture of sulfuranes at −40°. The reaction is so fast that local depletion of reagents at the point of addition of a drop of alcohol distorts the relative rate data. Only when alcohol vapors were allowed to diffuse slowly into a stirred solution of sulfuranes at −40° in an evacuated apparatus were accurate relative rates obtained.

The earlier noted[3] observation by nmr spectroscopy that exchange of the alkoxy ligands of **1** with added R_FOH is faster than exchange with R_FOK in the same solvent led us to postulate a dissociative mechanism for this ligand exchange.

The resolution available using 220-MHz ^{19}F nmr (Table III) allowed us to show that the rate response of the ligand exchange of **1** with R_FOH to substituent changes in the *S*-phenyl groups (ρ is approximately −3) is qualitatively that expected for this mechanism. This makes it very unlikely that the alternative mechanism,

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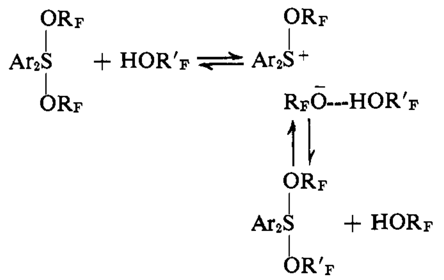
(17) (a) A. Rauk, L. C. Allen, and K. Mislow, *J. Amer. Chem. Soc.*, **94**, 3035 (1972); (b) J. B. Florey and L. C. Cusachs, *ibid.*, **94**, 3040 (1972); (c) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *ibid.*, **94**, 3047 (1972); (d) J. I. Musher, *ibid.*, **94**, 1370 (1972); (e) for a somewhat different view, see I. Ugi and F. Ramirez, *Chem. Brit.*, 198 (1972).

(18) D. P. Craig and E. A. Magnusson, *J. Chem. Soc.*, 4895 (1956).

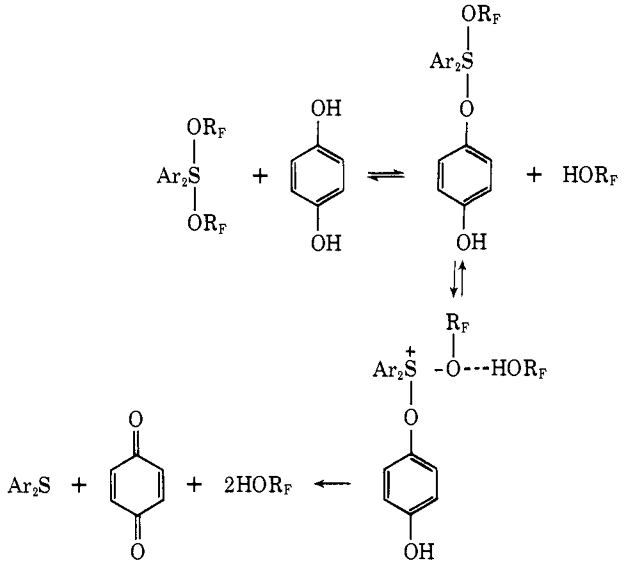
(19) E. F. Perozzi and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 5519 (1972); see I. Kapovits and A. Kálmán, *Chem. Commun.*, 649 (1971), for a related observation.

(20) M. Allan, A. F. Janzen, and C. J. Willis, *Can. J. Chem.*, **46**, 3671 (1968).

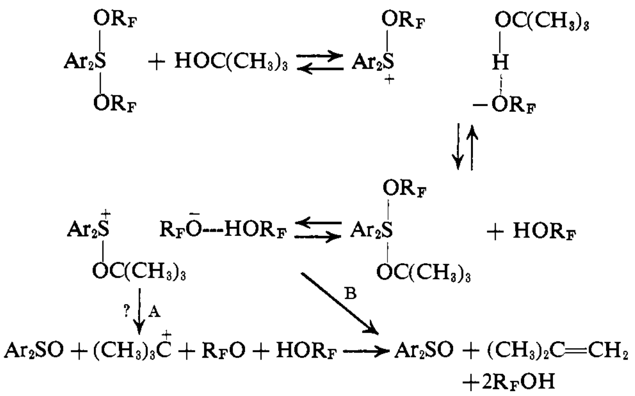


involving nucleophilic displacement on sulfur, is operative.

The pictured dissociative mechanism for ligand exchange has been used as a mechanistic model to rationalize or predict a large number of new reactions of sulfurane **1** with compounds containing O–H or N–H groups.[4] For example, the reaction with hydroquinone, which was used in the present work for the quantitative reduction of sulfuranes to the more volatile, less reactive sulfides before glpc analysis, was predicted upon the basis of a mechanism involving this ligand exchange in its first step. This reduction is probably mechanistically related to the much slower oxidation of hydroquinone to benzoquinone by dimethyl sulfoxide–dicyclohexylcarbodiimide in phosphoric acid.[21]



We suggest a closely related mechanism for the dehydration of *tert*-butyl alcohol.



Our competitive rate studies of this reaction determined a ρ value (-1.68) for substituent changes in the *S*-aryl group which requires a transition state more positively charged than the ground state. This could be the case for each of the steps in the pictured mechanism. The nature of the earlier reported[4] dependence of the rate of the reaction on alcohol structure, markedly slower for secondary alcohols, suggests that step A or B is probably rate determining.

The small kinetic isotope effect ($k_H/k_D = 1.54$) seen[4] in the product determining step for the dehydration of $CH_3C(CD_3)_2OH$ has been interpreted[4] in terms of a mechanism near the E1 end of the mechanistic spectrum. We would therefore suggest a rate-determining step resembling A but possibly modified by some minimal involvement of base with the incipient *tert*-butyl cation, as in reaction B leading directly to olefin.

The substituent effects are correlated with σ. In contrast, the basicities of substituted diphenyl sulfoxides are correlated[22] with σ^+. The protonated sulfoxide, with a full positive charge at the reaction center, must involve the electron-deficient sulfur to a more important degree in $p\pi$–$d\pi$ resonance with the electron donor aryl group. Earlier studies[23] of phenol acidities, using *p*-dimethylsulfonium substituents, arrived at a related conclusion. This suggests that the rate-determining step for the dehydration of *tert*-butyl alcohol by sulfuranes has considerably less than a full positive charge on sulfur in the transition state. The value of ρ (-1.68) is considerably smaller than the estimated value (-3) for the ligand exchange reaction, in keeping with this suggestion.

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(21) M. G. Burdon and J. G. Moffatt, *J. Amer. Chem. Soc.*, **88**, 5855 (1966).

(22) S. Oae, K. Sakai, and N. Kunieda, *Bull. Chem. Soc. Jap.*, **42**, 1964 (1969).

(23) F. G. Bordwell and P. J. Boutan, *J. Amer. Chem. Soc.*, **78**, 87 (1956).