Polarizability of the Hypervalent Bond in Some Unsymmetrically Substituted Sulfuranes as Reflected in Carbonyl Stretching Frequencies of Acyloxy Ligands[1]

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Abstract: Several acyloxy sulfuranes which are unsymmetrically substituted at the apical positions, compounds of the type **4** and **5**, have been prepared and their carbonyl stretching frequencies recorded. The position of the carbonyl absorption in the infrared spectrum is found to be extremely sensitive to the electronic nature of the ligand trans to an apical acyloxy group (varying from 1609 to 1832 cm^{-1}). Comparisons are made with other carbonyl-containing hypervalent molecules and with a series of model compounds in which the variable group is attached directly to the carbonyl carbon. The carbonyl frequencies of the sulfuranes are more responsive to variations in substituent than either of the model series. The effect is explained by invoking a significant contribution from resonance forms (**22**) providing a variable level of negative charge on the apical acyloxy group, which is reflected in a greater or lesser resemblance to a carboxylate anion in its carbonyl stretching frequency. The three-center four-electron apical bond is shown to be remarkably polarizable.

Sulfur is an element distinguished by the rich diversity of bonding arrangements in functional groups to which it is central. Types of sulfur-oxygen bonds, in particular, appear in a bewildering and growing array. While the electronic structures of the more prosaic functional groups containing S-O bonds (sulfoxides, sulfones, etc.) have been well-studied,[2] the three-center four-electron "hypervalent" [3] O-S-O bond has only recently received attention. Most of the hypervalent sulfur compounds studied to date have had either O-S-O or X-S-X (with X = F or Cl) bonds.

Insights into the structure of the hypervalent O-S-O bond have been provided by a number of approximate MO treatments of model or hypothetical sulfuranes,[4] including SH_4, SH_2F_2, and SF_4.

In addition to the extended Hückel calculations which have been reported,[5] studies using the CNDO/2 approach[6] and two levels of ab initio calculations[7,8] have been described. Although the latter two disagree as to whether the equilibrium geometry of SH_4 is of C_{4v} symmetry[7] or C_{2v} symmetry, all calculations are successful in describing the observed[9,10] greater negative charge on the apical fluorines of SF_4 relative to those in equatorial positions. This is in agreement with the simplest picture of hypervalent bonding originally proposed by Musher.[3]

All model systems so far studied theoretically have ligands which are identical at both apical sites. Structures such as **1** have not yet been considered. One might expect resonance forms **2** or **3** to be unequal contributors when the difference in electronegativity between X and Y is large. Setting our understanding of this ionic contribution on a quantitative, or even qualitative footing would be most helpful, both for the theorist seeking a deeper understanding of hypervalent bonding and the experimentalist who would like to be able to predict the chemical and spectroscopic properties of new sulfuranes.

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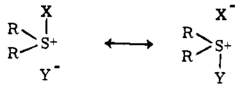
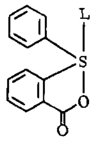


2 **3**

We have prepared a series of sulfuranes of the type **4** and **5** and recorded the position of the carbonyl infrared absorbance as a function of ligand L or Y–X. From these data, valuable insight into the nature of the hypervalent bond may be gained.



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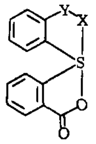

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Experimental Section

Ether and pentane were dried and stored over sodium wire. Methylene chloride and chloroform were distilled from P_2O_5 under nitrogen. NMR chemical shifts are reported in parts per million downfield from Me_4Si (the δ scale) for ^1H, in parts per million upfield from $CFCl_3$ for ^{19}F, and in parts per million downfield from Me_4Si for ^{13}C. Infrared spectra were obtained with a Perkin-Elmer Model 237B grating infrared spectrophotometer, using three polystyrene bands (1944, 1601, 1028 cm^{-1}) for calibration. Microanalyses, performed by Mr. J. Nemeth and associates, of the University of Illinois, were within 0.4% of the calculated values for the indicated elements.

2-[2-(2-Hydroxy-2-propyl)phenylthio]benzoic Acid (7a). In a modification of a published[11] method used for related compounds, equimolar amounts of *o*-iodobenzoic acid and 2-(2-hydroxy-2-propyl)thiophenol (**6a**)[12b] in an aqueous solution containing 2 equiv of KOH and a catalytic amount of copper bronze were boiled with stirring under N_2 for 21 h. The hot reaction mixture was filtered and the filtrate was quenched with dilute HCl and ice to give a white precipitate. Recrystallization from ether-pentane at −30 °C gave 7.52 g (50%) of **7a**, mp 115–116 °C: IR ($CHCl_3$): 3740 (m, br), 3000–2400 (characteristic carboxylic acid OH), 1678 (vs), 1587 (m), 1562 (m), 1464 (s), 1433 (m), 1406 (m), 1383 (m), 1364 (m), 1335 (w, br), 1309 sh plus 1287 (m, br), 1253 (s, br), 1037 (s), 945 (m), 850 cm^{-1} (m, br); ^1H NMR ($CDCl_3$) δ 1.71 (s, 3, CH_3), 6.7–8.2 (m, 8, aromatic CH). Anal. ($C_{16}H_{16}O_3S$): C, H, S.

3,3-Dimethyl-3′-oxo-1,1′-spiro[3*H*-2,1-benzoxathiole], Sulfurane 8a. To a solution of 84 μL of dry pyridine (1.04 mmol) and 0.302 g of **7a** (1.05 mmol) in 50 mL of dry $CHCl_3$ was added 119 μL of *tert*-butyl hypochlorite (1.05 mmol). This mixture was stirred occasionally for several minutes, washed twice with ice water, and dried over $MgSO_4$. The chloroform was removed to give 0.18 g (60%) of **8a**, a white solid, mp 205–205.7 °C (softens 202.5 °C): ^1H NMR ($CDCl_3$) δ 1.77 (s, 3, CH_3), 1.87 (s, 3, CH_3), 7.17–8.37 (m, 8, aromatic CH); IR ($CHCl_3$) 2960 (s), 1647 (vs), 1580 (m), 1445 plus 1464 sh (m), 1387 (m), 1368 (m), 1332 (s), 1299 (s), ~1030 (w), 943 (s), 860 (s), 830 (s), 680 cm^{-1} (w). Anal. ($C_{16}H_{14}O_3S$): C, H, S.

2-[2-(2-Hydroxy-1,1,1,3,3,3-hexafluoro-2-propyl)-4-methylphenylthio]benzoic Acid (7b). A solution of 2-(2-hydroxy-1,1,1,3,3,3-hexafluoro-2-propyl)phenylthiol (1.00 g, 3.45 mmol), *o*-iodobenzoic acid (0.85 g, 3.43 mmol), and KOH (0.50 g of 87.3% purity, 9.34 mmol) in 50 mL of water containing a catalytic amount of copper bronze was treated as described above for the preparation of **7a**. The crude precipitate was sublimed (180 °C (3.5 mm)) to yield 1.40 g (70%) of **7b**, mp 196.5-200 °C: ^{19}F NMR ($CHCl_3$) 74.66 ppm (s); IR ($CHCl_3$) 3344 (br, 2), 3000-2200 (CO_2H), 1686 (s), 1582 (w), 1560 (w), 1456 (m), 1399 (m), 1227 (vs), 1040 (m), 952 cm^{-1} (m). Anal. ($C_{17}H_{12}F_6O_3S$): C, H, S.

3,3-(Bis(trifluoromethyl))-3′-oxo-1,1′-spiro[3*H*-2,1-benzoxathiole], sulfurane 8b, was prepared in 62% yield by the procedure described for **8a** to give white crystals, mp 160-163 °C: ^{19}F NMR ($CHCl_3$) 73.77 (q, J = 9 Hz, 1.06), 76.85 (q, J = 9 Hz, 1.00) ppm; ^{1}H NMR (CCl_4) δ 2.50 (s, 3, CH_3), 7.28-8.30 (m, 7, aromatic CH); IR ($CHCl_3$) 2950 (w), 1708 (vs), 1600 (m), 1450 (m), 1176 (vs, br), 1111 (s), 1036 (m), 989 (m), 963 (s), 813 cm^{-1} (w). Anal. ($C_{17}H_{10}F_6O_3S$): C, H, S.

1-Chloro-1-phenyl-3-oxo[3*H*-2,1-benzoxathiole], Chlorosulfurane 10. 2-(Phenythio)benzoic acid was treated with 1 equiv of KOH in water. The solvent was removed and the solid residue was recrystallized from *n*-butyl alcohol, traces of water being removed as an azeotrope, affording potassium salt **11**. Anal. ($C_{13}H_9O_2SK$): C, H, S, K.

A suspension of **11** in CCl_4 was treated at room temperature with a stream of chlorine for 5-10 min. Filtration gave a solution exhibiting carbonyl bands in the infrared due to **10** (1740 cm^{-1}) and **35** (1792 cm^{-1}). Over the course of a day, the 1740-cm^{-1} band decreased in intensity, with a parallel increase in the intensity of the 1792-cm^{-1} band: ^{1}H NMR (CCl_4) δ 7.43 (s, aromatic), 7.50-8.58 (m, aromatic), 9.15 (m, CH ortho to S in **10**).[13]

In one experiment transparent crystals were deposited from the solution of **10** on standing for several days: ^{1}H NMR as above; IR (Nujol mull) 1790 (w), 1730 cm^{-1} (s). Anal. ($C_{13}H_9SO_2Cl$): C, H, S, Cl.

1-(Trifluoromethanesulfonyloxy)-1-phenyl-3-oxo[3*H*-2,1-benzoxathiole] (13). 2-(Phenylthio)benzoic acid (15.5 g, 67.3 mmol), prepared by the literature method,[11] in 80 mL of dry CH_2Cl_2 was treated with a stream of ozone at ambient temperature until the solution became faintly blue. After solvent removal, the residue was recrystallized from ethyl acetate to give 2-(phenylsulfinyl)benzoic acid (**12**), 12.1 g (73%), mp 164-165 °C, lit.[18] 164 °C.

To 2-(phenylsulfinyl)benzoic acid (**12**, 7.01 g, 28.5 mmol) suspended in dry ether under N_2 at −20 °C was slowly added 5.00 mL (28.5 mmol) of triflic anhydride, and stirring was continued 1 h. Filtration under N_2 (glove box) gave 10.49 g (97%) of **13**. Recrystallization from CH_2Cl_2-ether afforded crystals, mp 102-104 °C. The extreme water sensitivity of this material rendered analysis difficult. Anal. ($C_{14}H_9F_3S_2O_5 \cdot \frac{1}{2}H_2O$): C, H, S. ^{19}F NMR ($CH_2Cl_2$) 78.7 ppm (s), two alkoxy sulfonium triflates previously studied[19] appeared at 79.0 and 78.9 ppm; ^{1}H NMR showed no acid peak down to δ 13; ^{1}H NMR (220 MHz, CH_2Cl_2) δ 8.69 (d of d, J = 7, 1 Hz, 1.01, CH ortho to S on fused ring), 8.40 (d of d, J = 7, 2 Hz, 0.95, CH ortho to carboxyl), 8.18 (q of d, J = 7, 1.5 Hz, 1.96), 7.84 (q, J = 4.5, 1.00), 7.66 and 7.64 (2s, 4.07).

***tert*-Butyl *o*-(Phenylsulfinyl)benzoate (39).** Freshly sublimed potassium *tert*-butoxide (0.44 g, 3.92 mmol), in 30 mL of dry ether, was treated with 1.02 g (4.10 mmol) of *o*-(phenylthio)benzoyl chloride[20a] in small portions. The resulting mixture was stirred for 5 h at room temperature and filtered. Removal of ether yielded a yellow oil which gave a ^{1}H NMR (C_6H_5Cl) singlet δ 1.57 (s, $(CH_3)_3C$).

The oil was diluted with methylene chloride and ozone passed through this solution at room temperature until the reaction mixture acquired a blue-grey color. Removal of solvent left a brown oil, which after column chromatography (basic alumina, ether eluent) afforded a viscous yellow liquid showing one singlet in the ^{1}H NMR at 1.41 ppm (chlorobenzene solvent). The absence of additional *tert*-butyl resonances indicates the sulfide was oxidized cleanly to the sulfoxide, and sulfone was not formed.

Reactions of 1,1-Dichloro-3-oxo[3*H*-2,1-benzoxathiole]. Dichlorosulfurane 36. The dichlorosulfurane was prepared according to the literature[14] method, with the exception that volatile products and solvent were removed in vacuo: ^{1}H NMR (CH_2Cl_2) δ 7.83-8.23 (m, 1, CH ortho to carbonyl); 8.35-8.63 (m, 1, CH ortho to S); ^{13}C NMR ($CDCl_3$) 123.4, 132.7, 134.0, 135.4 (aromatic CH), 128.4, 150.9, 166.0 ppm (quaternary C); IR (Nujol mull) 1790 (m), 1730 (s), 1690 cm^{-1} (w). Dichlorosulfurane **36** may also have the structure of the isomeric *o*-(chlorosulfinyl)benzoyl chloride.[15,16]

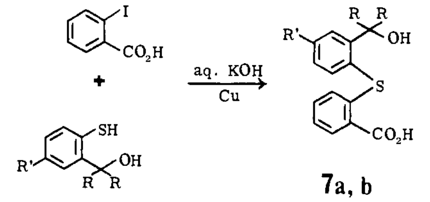
Perfluoropinacol[13] (95 μL, 0.54 mmol) was mixed with dichlorosulfurane **36** (120 mg, 0.54 mmol), and methylene chloride, previously dried over solid KH, was added. To this, a large excess of solid KH was added slowly. The reaction mixture was filtered: ^{19}F NMR (CH_2Cl_2) 64.64 (br m, 1), 66.02 (br m, 2.6, CF_3), 67.23 ppm (very br m, 9.2). The very broad peaks at 66.02 and 67.23 are very similar to those seen for other sulfuranes with this ligand spanning apical-equatorial sites.[17]

Addition of the potassium salt of 1,1,1,3,3,3-hexafluorocumyl alcohol (KOR_F) to the dichlorosulfurane in methylene chloride, followed by filtration, gave a solution whose ^{19}F NMR spectrum consisted of a singlet at 75.69 ppm (hexafluorocumyl alcohol) and a symmetrical multiplet at 70.94 ppm (relative to $CFCl_3$). A very small multiplet was in evidence at 69.70 ppm. When this experiment was done in ether, a symmetrical multiplet in the ^{19}F NMR appeared at 70.12 ppm, a broad peak with some fine structure at 70.97, and a sharp singlet at 75.15 ppm. Addition of KOR_F to this solution served to broaden the upfield resonance and shift it to 75.65 ppm, and caused more fine structure to become apparent in the 70.97 signal. In a separate experiment (ether solvent) addition of H_2O to the product solution caused the low-field set of signals to collapse to a singlet at 70.21 ppm, the high-field singlet remaining sharp at 75.25 ppm. Addition of *tert*-butyl alcohol to a solution of the product in methylene chloride caused the ^{19}F NMR spectrum to appear as a singlet at 75.23 ppm. Treatment with *tert*-butyl alcohol produced isobutylene, detected by ^{1}H NMR, and a product exhibiting a singlet in the ^{1}H NMR at 1.6 ppm.

Results and Discussion

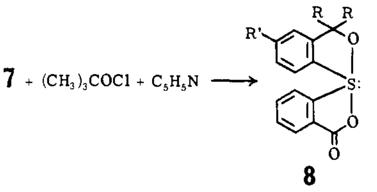
Syntheses of Sulfuranes and Model Compounds. The general route to the spirobicyclic sulfuranes is outlined in Scheme I.

Scheme I



7a, b

6a R = CH_3, R′ = H
6b R = CF_3, R′ = CH_3



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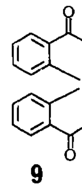
Sulfurane **9** was prepared by the literature method[20b] and was freshly sublimed before use. Chlorosulfurane **10** was prepared by treatment of a suspension of **11** in CCl_4 with excess chlorine. Reaction of 2-(phenylsulfinyl)benzoic acid (**12**) with trifluoromethanesulfonic (triflic) anhydride (TfOTf) afforded acyloxysulfonium triflate **13**.



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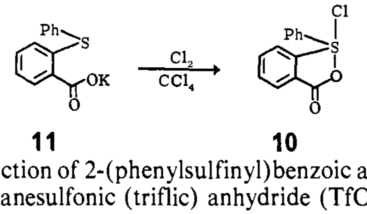
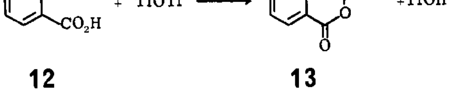
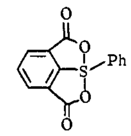


11 **10**



12 **13**

The synthesis of **14** via thermolysis of a bis(perester) has been described.[21]



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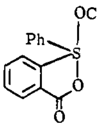
Sulfurane **15** was prepared by reaction of **11** with 1 mol of *tert*-butyl hypochlorite, as previously described.[22] Salts **16** and **17** were not isolated, but prepared on a small scale from chloroform solutions of the corresponding acids by the addition of triethylamine.[23]



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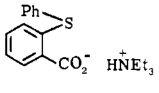

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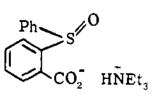

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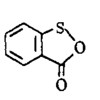
Carbonyl Stretching Frequencies. The carbonyl stretching frequencies in the series of sulfuranes listed in Table I are very responsive to changes in the nature of the trans apical substituent. Consider sulfurane **9** (or **14**) as the reference compound in the series. How may we rationalize the position of **9** in this listing of carbonyl frequencies? Field, Giles, and Tuleen[24] report a carbonyl frequency of 1790 cm^{-1} for a compound thought to have structure **18**. An acyclic analogue **19**, absorbs at 1775 cm^{-1}.[25] Phthalide (**20**) absorbs at 1778 cm^{-1}.[26] On the basis of these models, one might have predicted that **9** would absorb in the region 1770-1790 cm^{-1}. However, the observed 1724 cm^{-1} is well-removed from this range. Quantum mechanical calculations of several types[6-8,27] predict substantial electron density on the apical ligands. If this is expressed in resonance terms, viz. **21**, it provides a rationale for the unexpectedly low carbonyl stretching frequency seen for **9**.



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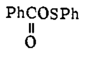
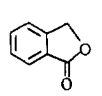


$PhC(=O)SPh$

19



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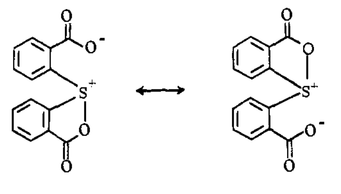


21a **21b**

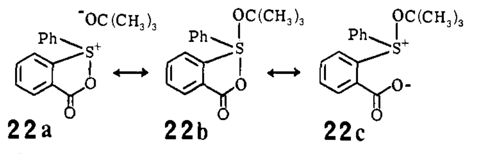
Carboxylate anions, such as **16** or **17**, absorb in a range at the low frequency end of the carbonyl stretching region. The "shift" of **9** to lower frequency relative to the structurally similar (but electronically unrelated) compounds **18**-**20** is in a direction consistent with the postulation of a significant amount of carboxylate character in **9**. If **18**-**20** are valid as models, the IR carbonyl frequency of **9** points to the charge-separated resonance forms **21** as nontrivial contributors to the electronic complexion of **9**.

Consider sulfurane **15** (or **8a**). Here the carbonyl stretch is nearly *in* the carboxylate region, leading to the conclusion that there is even more carboxylate character in these molecules than that ascribed to **9**. Moreover, the conclusion that **15** has considerable carboxylate character is independent of how much carboxylate character is ascribed to **9**. Again, in resonance terms, one may posit **22c** to be of major significance relative to **22b**, and **22a** to be of little significance relative to **22c**.

Table I. Carbonyl Stretching Frequencies of Acyloxysulfuranes as a Function of Trans-Apical Ligand Identity

	Trans ligand		
Compd	L (in **4**)	X-Y (in **5**)	$\nu_{C=O}$, cm^{-1} (in $CHCl_3$)
16	"electron pair" [a]		1609
17	$-O^-$ [a]		1613
15	-O-*t*-Bu		1640
10	-Cl		1740
13	$-OSO_2CF_3$ [b]		1832 (1821 sh)
8a		$-C(CH_3)_2O-$	1647
8b		$-C(CF_3)_2O-$	1708
9		-COO-	1724
14			1722[c]

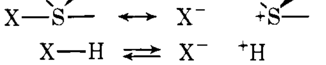
[a] If these carboxylates were to exist as the ring tautomers, the listed L groups might formally be considered to be apical ligands. [b] Probably the ionic sulfonium triflate. [c] Reference 21b.



22a **22b** **22c**

The other compounds in the series may be rationalized similarly. If the acyloxy group of **4** or **5** is more "electronegative" than L or X-Y, electron density will accumulate at the acyloxy terminus of the hypervalent O-S-O′ bond, conferring carboxylate character and shifting the carbonyl frequency to lower than 1724 cm^{-1}. Conversely, if L or X-Y is the more electronegative apical ligand, the O-S-O′ bond is polarized in the opposite sense (e.g., **22a**), and the carbonyl stretching frequency is increased. The limiting case of polarization in this sense is given by acyloxysulfonium salt **13**, which absorbs at 1832 cm^{-1}. The geometry of **13** is probably distorted tetrahedral, perhaps significantly different in geometry from the TBP sulfuranes with which it is compared.[28] Thus when L or X-Y is more electronegative than the acyloxy group, the carbonyl frequency moves to frequencies higher than 1724 cm^{-1}. Another example of this sense of O-S-O′ polarization is chlorosulfurane **10**.

Electronegativity, in the context of this discussion, has taken on the rather special meaning of the ability of a sulfurane apical ligand to affect the carboxylate character of an acyloxy group trans to it. Might this property be related to any of the more familiar indices of electronegativity? One might suggest that the extent of the polarization of the O-S-X hypervalent bond (eq 1) is related to the equilibrium constant for ionization of H-X (eq 2); what we have called electronegativity might parallel the pK_a's of the conjugate acids of the various ligands.



$$X{-}S{-} \longleftrightarrow X^- \quad {}^+S{-} \qquad (1)$$

$$X{-}H \rightleftharpoons X^- \quad {}^+H \qquad (2)$$

According to this notion, the acyloxy ligand of **9** would be modeled by *o*-(phenylthio)benzoic acid, pK_a = 4.17 (see Table II).[29] The model for the chlorine ligand of **10** is HCl. A recent measurement of the pK_a of HCl yields a value of −3.7.[33] The unavailable pK_a of cumyl alcohol would be required to model the cumyloxy ligand of **8a**. An approximate value can be estimated as follows; the effect of replacement of H by CH_3 in the series CH_3OH (pK_a = 15.2,[32] 15.09[31]), $(CH_3)_2CHOH$ (pK_a = 15.7,[32] 17.1[31]) should be mirrored on going from benzyl alcohol (pK_a = 15.4[31]) to cumyl alcohol. Thus, the pK_a for cumyl alcohol should be in the range 15.9-17.4. The effect of replacing H by C_6H_5, as from CH_3OH (pK_a = 15.09) to benzyl alcohol (pK_a = 15.4) provides another basis for esti-

Table II. pK_a Values for Model Conjugate Acids of Trans-Apical Ligands

Sulfurane	Ligand model	pK_a
9	*o*-$PhSC_6H_5CO_2H$	4.17[a]
8b	$PhC(CF_3)_2OH$	8.8–9.5[b]
	$HC(CF_3)_2OH$	9.3[c]
8a	$PhC(CH_3)_2OH$	15.9–17.4[b]
15	$(CH_3)_3COH$	15.0,[e] 19.2[d]
	$PhCH_2OH$	15.4[d]
10	HCl	−3.7[f]

[a] Calculated from data in ref 29. [b] Estimated, see text. [c] Reference 30. [d] Reference 31. [e] Reference 32. [f] Reference 33.

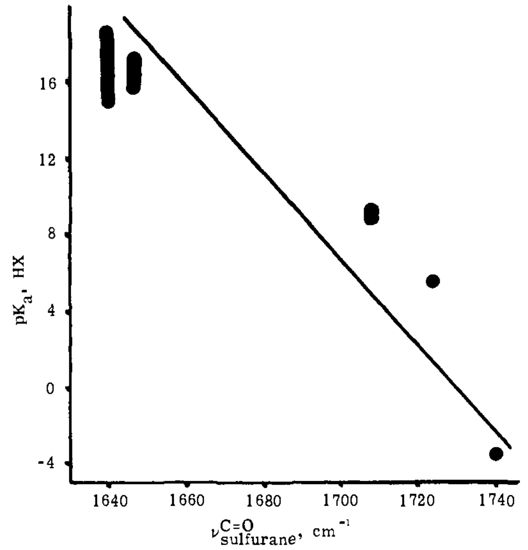


Figure 1. Plot of pK_a values for HX (Table II) against carbonyl stretching frequencies (Table I) of acyloxysulfuranes with apical X ligands trans to the acyloxy ligand.

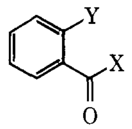
mating the pK_a of cumyl alcohol from the pK_a of 2-propanol. This approach provides an estimated pK_a for cumyl alcohol of 15.9–17.3, in good agreement with the earlier estimate. A reasonable guess for the pK_a of 1,1,1,3,3,3-hexafluorocumyl alcohol (9.5) can also be based on the effect (0.2 pK_a units) of replacing H by C_6H_5, since 1,1,1,3,3,3-hexafluoro-2-propanol has been reported[30] to have a pK_a of 9.3. Alternative methods of estimating the pK_a of hexafluorocumyl alcohol give values in the range 8.8–8.9.[34]

Figure 1 shows a satisfactory correlation of pK_a's of the conjugate acids of the trans ligands with carbonyl stretching frequencies of the sulfuranes. One would not expect a close correlation, since π-type bonding to sulfur would be expected to play a role in sulfuranes, such as these, with ligands having accessible p orbitals, and a different sort of π interaction affects the pK_a of acids.

An attempt to correlate the stretching frequencies with σ_I was less successful because of the paucity of accurate model substituents for which σ_I is known.

Although little is known of the apicophilicities of substituent groups in sulfuranes,[38] one can presume, in line with those observations which have been made,[39] that the more "electronegative" substituents will be apical, as is seen in the phosphoranes, and as is implied by the sulfurane MO calculations. It is conceivable that the ability of an apical ligand in a sulfurane to shift the carbonyl stretching frequency of a trans acyloxy group will be related to the tendency of the ligand to occupy an apical position. More work will be needed before one can assess the utility of sulfurane carbonyl frequency shifts in rationalizing the structural chemistry of sulfuranes.

Table III. Carbonyl Stretching Frequencies of Model Compounds Related to the Sulfuranes of Table I in Having Comparable Ligands Directly Bonded to Carbonyl Carbon



X	Y	$\nu_{C=O}$, cm^{-1}
$OC(CH_3)_3$	SPh	1709
$OC(CH_3)_2Ph$	H	1715[a]
$OC(CF_3)_2Ph$	SPh	1746[b]
o-$PhSC_6H_4CO_2$	SPh	1785, 1720[c]
Cl	SPh	1760, 1724

[a] Reference 40b. [b] Reference 42. [c] Reference 43.

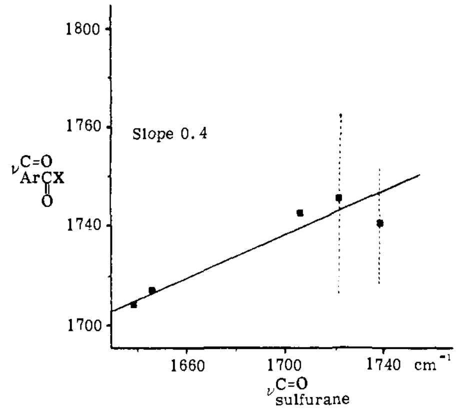
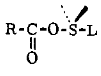


Figure 2. Correlation of the data of Table III with values of $\nu_{sulfurane}^{C=O}$ from Table I, listed in order of increasing frequency: **4** (X = OtBu), **5** (X = $-C(CH_3)_2O-$), **5** (X = $-C(CF_3)_2O-$), **5** (X = COO–), and **4** (X = Cl). For the latter two points the correlation is with carbonyl stretching frequencies for an acid chloride and a carboxylic acid anhydride, each of which shows two peaks in the carbonyl stretching region (at the extremes of the dotted lines). The points shown are for average values of these two peaks.

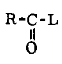
In a formal sense, the sulfuranes may be considered "sulfinylogues" of the corresponding acyl compounds ArCOX, e.g., **16** would be the "sulfinylogue" of *tert*-butyl *o*-(phenylthio)benzoate. Table III lists $\nu_{C=O}$ for a series of appropriate model compounds based on this notion. The low value for the *tert*-butyl ester is in line with $\nu_{C=O}$ of other *tert*-butyl esters.[40] Double peaks are seen in the carbonyl stretching region for both *o*-(phenylthio)benzoyl chloride (Fermi resonance)[41] and *o*-(phenylthio)benzoic anhydride (in-phase and out-of-phase carbonyl stretching).

In order to compare *o*-(phenylthio)benzoyl chloride and *o*-(phenylthio)benzoic anhydride with **10** and **9**, we have shown the average of the two frequencies for each of these compounds on the plot of Figure 2. This plot shows the correlation of the sulfurane carbonyl stretch (Table I) with that of the acyl-X model compound (Table III) with a slope of 0.40. That is, within the limits imposed by the aptness of the models and the meager number of points used to construct the line, one may conclude that interposition of a hypervalent bond between carbonyl and ligand L renders the carbonyl group stretching frequency roughly twice as sensitive to the electronic nature of L as in the directly bonded analogue. The carbonyl stretching frequency of **23** is twice as responsive to change of L as is that of **24**.



$$R-\underset{\underset{O}{\|}}{C}-O-S-L$$

23



$$R-\underset{\underset{O}{\|}}{C}-L$$

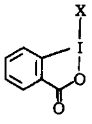
24

Table IV.[a] Iodinane Stretching Frequencies

X in **25**	$\nu_{C=O}$, cm^{-1} [b]	Compare to
-OCH$_3$	1673	**16**
-OEt	1667	**16**
-OBu-*n*	1666	**16**
-OC(=O)CH$_3$	1692	**9**
-OC(=O)Ar[c]	1696-1698	**9**
-Cl	1698	**10**

[a] Data from ref 44. [b] In CHCl$_3$. [c] Ar = C$_6$H$_5$, *o*-BrC$_6$H$_4$, *o*-FC$_6$H$_4$, *o*-IC$_6$H$_4$, *o*- and *m*-ClC$_6$H$_4$.

Comparisons with Other Hypervalent Species. Etter[44] has recently reported carbonyl stretching frequencies for hypervalent iodine compounds ("iodinanes") of the type **25**. These

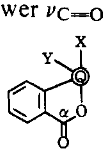


25

are reproduced in Table IV.

Here, the trend in carbonyl shift on going from alkoxy to acyloxy to chloro axial ligand observed in the sulfurane series is preserved, but the 100-cm^{-1} range of the sulfuranes is compressed to only 32 cm^{-1} in the iodinanes. Also, the "center of gravity" of the series of iodinane frequencies is qualitatively at lower frequency than that of the sulfuranes. This suggests that the iodinanes (**25**) as a class may resemble iodonium carboxylates more than the sulfuranes (**4** and **5**), as a class, resemble sulfonium carboxylates.

Another possible reason for the compression and bathochromic translation of the iodinane frequency range is the difference in geometry about the carbonyl carbon in the acyloxy iodinanes vs. the corresponding sulfuranes. As the covalent radius *Q* increases in **26**, angle α would also increase if the five-membered ring were to maintain planarity. This might be expected[45] to lower $\nu_{C=O}$.



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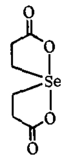
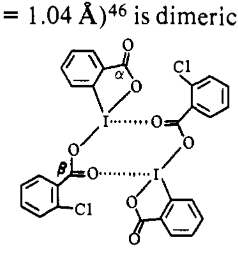


27

Data for model compounds suitable to test this prediction are not easy to find. Selenurane **27** (Q = 1.14 Å)[46] absorbs at 1675 cm^{-1} compared to 1724 cm^{-1} for the somewhat analogous sulfurane **9**.[47] Noting that the conjugation of the carbonyl groups of **9** with the aryl rings, an interaction absent in **27**, would be expected[45] to lower the frequency for **9**, the difference would be even greater than the observed 47 cm^{-1} in a more perfect model. The difference is in the direction predicted for the angle strain effect postulated above.

These data are misleading, however, since the $\nu_{C=O}$ value for **27** was obtained from a KBr disk, and lattice interactions can be important determinants of $\nu_{C=O}$. For example, the "α" crystalline form of 3-oxo-3*H*,2,1-benzoxiodol-1-(3′-chlorobenzoate) (**28**) (Q = 1.04 Å)[46] is dimeric, as shown.[44] While the angle β is 118°, $\nu_{C=O}$ (KBr) for the exocyclic carbonyl is 1618 cm^{-1}, lowered by intermolecular interaction with trivalent iodine, 2.96 Å distant. The ring carbonyl appears at 1689 cm^{-1} (KBr); angle α is 115°. In CHCl$_3$ solution, only one carbonyl absorption, at 1696 cm^{-}, is seen. In solution, α and β are, of course, not known precisely, but the value of $\nu_{C=O}$ is lower than for **9** as predicted. The internal CC(=O)O angle in sulfurane **9** is reported to be 112.5 ± 2.2°.[48] Perhaps unexpectedly, the analogous angle α in selenurane **29** is reported to be 112.1 ± 0.07°,[49] and in **30**, α = 113.7 ± 0.03°.[50]



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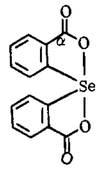

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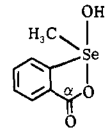
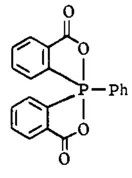


30

Musher[52] has reported a series of hypervalent antimony compounds (Q = 1.36)[46] of the type Ph$_3$Sb(O$_2$CR)$_2$ to have $\nu_{C=O}$ in the range 1621-1678 cm^{-1}. Although the range is similar to that seen for the iodinanes, the fact that the measurements were made using KBr pellets again makes comparison difficult. Phosphorane **31** (Q = 1.10)[46] a close analogue of sulfurane **9** absorbs at 1730 cm^{-1}.[53] The analogous **32**,[54] which has an alkoxy ligand trans to an unconjugated acyloxy group, absorbs at a very similar frequency, 1735 cm^{-1} (KBr). These values may be rationalized by invoking the x-ray PES results of Thomas et al.,[10] which indicate that equatorial and axial ligands are more nearly equivalent (in terms of charge distribution) in PF$_5$ than in SF$_4$. Thus the axial ligands of **31** are more "covalent" (less "ionic") than those of **9**. We recognize that other effects may be operative here, since models with which to compare **31**, as **9** was compared with **18**–**20**, are lacking. This renders our interpretation tentative.



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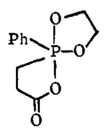

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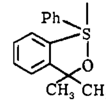
Thus, evidence in the structural literature concerning the possible dependence of $\nu_{C=O}$ upon the covalent radius Q in **26** is ambiguous, at least in part because of the uncertainties in extrapolating bond angles observed in crystals to the liquid phase. This leaves the postulated bond angle dependence on Q a possible, though unsubstantiated, factor in the observed differences between sulfurane and iodinane carbonyl stretching frequencies. The identical electronegativities of iodine and sulfur (2.5) on the Pauling scale[51] make it difficult to devise an argument based on a difference in electronegativities. Further work on this question is indicated.

Chemical Shift Evidence of Polarizability. Sulfuranes of the structure **33** have ^{1}H NMR spectra with two singlets corresponding to the two methyl groups. Table V shows how the average of the positions of the two methyl signals responds to changes in X. A shift to lower field (i.e., increasing δ) may be interpreted in terms of increasing polarization of the hypervalent bond in the sense of resonance structure **34** as X becomes more electronegative. The limiting case is provided by the salts **34**, X = BF$_4$, and **34**, X = OTf, both at δ 1.76.



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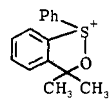

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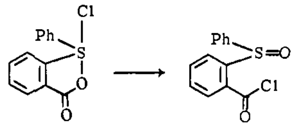
Table V. Methyl Proton Chemical Shifts for **33**[a]

X	Average of methyl shifts, δ[b]
$-OCH_3$	1.19
-CN	1.23
-OAc	1.30
$-N_3$	1.42
-Cl	1.47
34, X = BF_4	1.76
34, X = O_3SCF_3	1.76

[a] Reference 12a. [b] $CDCl_3$ solvent.

It is, therefore, clear that the polarizability of the unsymmetrical O-S-O′ or O-S-X hypervalent bond is not contingent on the presence of an acyloxy axial ligand.

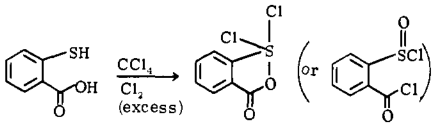
Chlorosulfurane 10 and Related Compounds. Chlorosulfurane **10** rearranges in solution at room temperature to sulfoxide acid chloride **35** over a period of days.



10 **35**

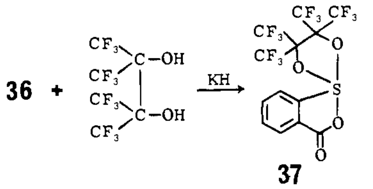
The rearrangement appears to be catalyzed by chlorine, which is usually present after preparation of **10**.

The related dichlorosulfurane **36** is prepared by reaction of chlorine with thiosalicylic acid.[14] The product of this reaction was postulated by Price and Smiles in 1928 to have the structure of dichlorosulfurane **36a**. More recent studies,[15,16] primarily of products of reaction of **36** with a variety of substrates, have favored structure **36b** for this compound.



36a **36b**

Two reactions of **36** thought to give cyclic analogues of **36a** were carried out in this work. Reaction with perfluoropinacol in the presence of excess KH produces a compound whose ^{19}F NMR spectrum gives evidence for structure **37**. Chemical shifts and peak shapes are very similar to those seen in low-temperature spectra of a closely related tetraoxysulfurane, which were reported earlier.[17b]



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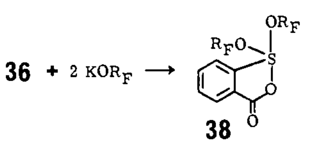
On the basis of NMR evidence involving comparisons with several closely related compounds,[1,13] the product of reaction of **36** with $KOC(CF_3)_2Ph$ (KOR_F) is thought to be **38**. Dialkoxysulfurane **38** was not, however, isolated.



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These experiments, like earlier ones[14-16] which provided structures for products of the reactions of **36** with various substrates, cannot provide the basis for an unequivocal choice between structures **36a** and **36b**. Since products **37** and **38**, like certain products reported by Price and Smiles,[14] point to **36a** as a possible structure, while other products[15,16] are more easily accounted for on the basis of **36b**, we must consider the possibility of a mobile equilibrium between these two structures for **36**.

In recent years a large number of sulfuranes have been prepared in our laboratory which can serve as models for **36a**. Studies of these compounds have provided some generalizations which favor, when applied to the spectroscopic data for **36**, structure **36a**. In particular, the ^1H NMR spectrum shows a low-field multiplet at δ 8.31-8.63 in a region which has been found to be characteristic for protons ortho to sulfur in cyclic sulfuranes. Although a peak of moderate intensity is seen at 1790 cm^{-1} in the infrared spectrum of **36**, a frequency which one might expect for the carbonyl stretch of acyl chloride **36b**, the strong absorption at 1730 cm^{-1} might more appropriately be ascribed to sulfurane **36a**.

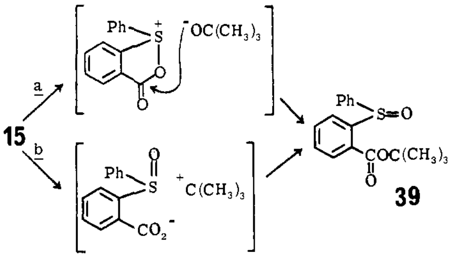
We would therefore suggest that **36** is probably an equilibrium mixture of **36a** and **36b**, containing a preponderance of the extraordinarily stable dichlorosulfurane tautomer (**36a**).

Conclusion

Sulfuranes of types **4** and **5** show a remarkable sensitivity of carbonyl stretching frequency to the identity of trans apical ligand. Qualitatively, these sulfurane carbonyl frequencies are considerably more responsive to changes of ligand than the corresponding compounds ArCOX, where the ligand is directly bonded to the carbonyl function. We interpret this phenomenon in terms of a varying contribution from polar resonance forms (**22**) reflecting an extraordinary polarizability of the three-center four-electron bond.

Armed with the notion of unsymmetrical sulfuranes as polar species, and with a good idea of the direction and some idea of the magnitude of polarization of the unsymmetrical hypervalent bond, the sulfurane chemist may begin to rationalize some of the chemistry of these compounds.

For example, one of the products of thermolysis of **15** is *tert*-butyl *o*-(phenylsulfinyl)benzoate (**39**).[22] Two pathways might be envisioned, as shown. However, its 1640-cm^{-1} carbonyl stretch confirms that **15** is polarized in a sense which suggests a preference for pathway b.



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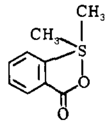
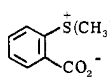
A sulfurane having an axial alkyl group trans to an acyloxy group might be predicted to be zwitterionic. In fact, **40** shows one singlet at δ 3.13 (alkaline D_2O) in its NMR spectrum,[55] very close to the δ 3.22 peak seen for the methyls of phenyldimethylsulfonium nitrate in D_2O.[56] It would appear that **40b** is the more correct formulation for this "sulfurane."



40a



40b

Trigonal bipyramidal species with first-row elements in the central position are commonly encountered as transition states.

For example, the transition state for the S_N2 reaction puts carbon in the center of a three-center four-electron hypervalent bond. It has not been possible to isolate or to observe such species directly.[57] If in fact such species are transition states, the deformation from the symmetrical geometry of the energy maximum to the unsymmetrical geometry of either ground state involves breaking one bond to the central atom as the other is shortened to form a two-center two-electron bond. Among those hypervalent derivatives of second and higher row nonmetallic elements which are isolable, the more stable are those further to the left and bottom of the periodic table.[58] Both phosphoranes and selenuranes appear to be more stable than sulfuranes. The greater sensitivity of the carbonyl stretching frequencies of acyloxy ligands in sulfuranes to variation in trans ligand than that seen for phosphoranes and selenuranes may be considered a reflection of the greater tendency for the less stable hypervalent bond of the sulfuranes to distort under unsymmetrical apical ligand fields in the mode of the transition states which have first row elements in the central position. The apical bonds to phosphoranes and selenuranes, being more covalent, are less easily distorted by such influences.

Acknowledgment. This work was supported by the National Cancer Institute, Grant No. CA-13963.

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