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Isolable Oxysulfuranes in Organic Chemistry

Many new types of isolable tetracoordinate organosulfur(IV) species are now available.

J. C. Martin and Edmund F. Perozzi

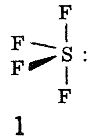
Compounds of sulfur(IV) in which four ligands are attached to sulfur have in common with the rare gas compounds, such as XeF_2, an electronic structure involving a formal expansion of the valence shell of the central atom from eight to ten electrons. We call such compounds sulfuranes (*1*); in this article we discuss those sulfuranes (*2*), only recently available for study, that have oxygen-centered ligands attached to sulfur. The incorporation of oxygen ligands makes possible a wide range of new structural types that illustrate structure-reactivity relationships in a particularly illuminating way.

The possible importance of oxysulfuranes and related species in organic chemistry was highlighted before their isolation by numerous lines of evidence (*3*) pointing to their involvement as high energy intermediates in reactions of sulfoxides, sulfonium ions, and sulfides.

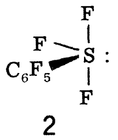
Halosulfuranes

Until recently the evidence for most types of sulfuranes postulated as intermediates was only indirect. The outstanding exception to this generalization is the class of sulfuranes with halogen ligands to sulfur. The halosulfuranes have been known as isolable compounds for many years. The preparation of the very unstable SCl_4 by Michaelis and Schifferdecker (*4*) in 1873 was followed in 1911 by the discovery (*5*) of the thermally stable but reactive sulfurane SF_4 which was not, however, fully characterized until 1929 (*6*, *7*). This was the forerunner of a whole family of stable fluorosulfuranes, derivatives of SF_4 in which one or two fluorines have been replaced by aryl or perfluoroalkyl groups (*8*–*10*).

The geometry of SF_4 (**1**), as determined by microwave spectroscopy (*11*) and electron diffraction (*12*), can be described as distorted trigonal bipyramidal with two fluorines and the lone pair of electrons occupying equatorial positions, with the other two fluorines in apical positions.



1



2

A substituent less electronegative than fluorine, such as the pentafluorophenyl group of **2**, shows a strong preference for an equatorial position in competition with fluorine (*10*) in accord with the general rules describing orders of apicophilicity in pentacoordinate compounds, which were enunciated several years ago (*13*).

The chlorosulfuranes are, in general, less stable thermally than their fluoro analogs. The treatment of sulfur(II) species such as diaryl sulfides with chlorine gives an adduct dichlorosulfurane, **3**, in a reversible reaction which maintains an appreciable vapor pressure of Cl_2 over the dichlorosulfurane at room temperature (*14*).

$$Ar_2S + Cl_2 \rightleftarrows Ar_2SCl_2$$

3

At temperatures below −30°C, however, such compounds as SCl_4 (*4*), CH_3SCl_3 (*15*), and $(p\text{-}ClC_6H_4)_2SCl_2$ (*16*) are stable. An x-ray crystallographic structure for the latter showed it to be covalent in the crystal with

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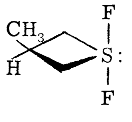
a distorted trigonal bipyramidal geometry (*16*) similar to that of SF_4, with equatorial phenyl ligands and apical chlorines.

Direct fluorination of simple dialkyl sulfides, with the recently developed (*17*) reagent CF_3OF as a fluorinating agent, has provided access to simple difluorosulfuranes such as **4** and tetrafluoropersulfuranes such as **5**. The latter, a hexacoordinate sulfur(VI) species, is a derivative of the very stable octahedral SF_6, a class of hypervalent sulfur compounds which we will follow Musher (*1*) in calling persulfuranes.



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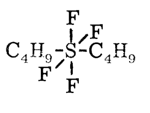


$$C_4H_9SF_4C_4H_9$$

5

Carbon Ligands

The treatment of triphenylsulfonium salts with phenyllithium was reported by Wittig and Fritz (*18*) in 1952 to result in the formation of biphenyl and diphenyl sulfide. The possibility that this reaction proceeded via the high energy intermediate tetraphenylsulfurane received support in isotopic tracer experiments of Harrison, Weston, Jacobus, and Mislow (*19*), which showed that all of the phenyl groups became equivalent en route to the products biphenyl and diphenyl sulfide (*20*).

$$\mathrm{Ph_3S^{\oplus} + PhLi \longrightarrow Ph\text{-}Ph + PhSPh}$$

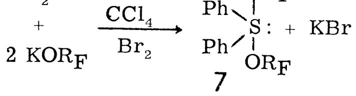
A similar route was used by Sheppard (*21*) to prepare the only isolated sulfurane with four carbon-centered ligands *tetrakis*-(pentafluorophenyl)sulfurane, (**6**), by the reaction of SF_4 with pentafluorophenyllithium. Compound **6** is stable at low temperatures but decomposes at 0°C to yield the expected diaryl sulfide and perfluorobiphenyl.

$$(C_6F_5)_4S$$

6

Oxysulfuranes

In 1971, the preparation of the first isolable diaryldialkoxysulfurane (**7**) was reported from our laboratory (*22*). This crystalline ketal analog of a sulfoxide proved to be stable indefinitely at room temperature when protected from moisture.



$$\mathrm{Ph_2S} + 2\,\mathrm{KOR_F} \xrightarrow[\mathrm{Br_2}]{\mathrm{CCl_4}} \mathrm{Ph_2S(OR_F)_2} + \mathrm{KBr}$$

7

[where $OR_F = OC(CF_3)_2Ph$]

$$7 + H_2O \longrightarrow 2\,R_FOH + Ph_2SO$$

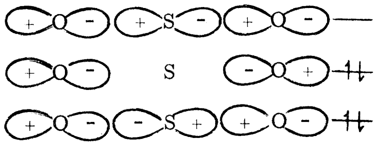


Fig. 1. Approximate molecular orbital model for the O-S-O hypervalent bond.

The hydrolysis of **7** is extremely rapid in moist air. A study of the reactions of **7** established it as a powerful and versatile reagent in organic chemistry. The dehydration of secondary and tertiary alcohols under particularly mild conditions (*23*), the facile cleavage of secondary amides (*24*), the conversion of primary amines to sulfilimines (*25*), and the single step cyclodehydrations of diols to give cyclic ethers (*26*) are reflections of an unusual pattern of reactivities which will be reviewed elsewhere (*27*).

Kapovits and Kálmán independently reported (*28*) a result similar to ours (*22*) on the preparation of the stable diaryldiacyloxysulfurane, **8**. This spirosulfurane appears to be much less reactive toward water (*28*) than is its acyclic analog **7**.

Two tetraoxysulfuranes have been reported, the water-sensitive tetraphenoxysulfurane **9** (*29*) and the difficultly hydrolyzable spirosulfurane **10** (*30*).

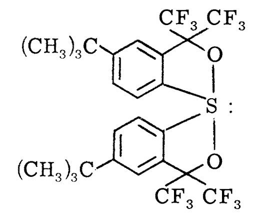
The greater stability of spirosulfuranes is dramatically illustrated by our observation (*31*) that spirosulfurane **11**, in sharp contrast to its acyclic analog **7**, does not hydrolyze. Attempts to prepare sulfoxide diol **12** by other methods give only the ring-closed product **11**.

The hydrolytic stability of sulfurane **11** is matched by that of spirosulfurane oxide **13**, a ketal analog of a sulfone, which is easily accessible by oxidation of **11** (*31*). This compound is not hydrolyzed upon extended heating with aqueous base or acid.

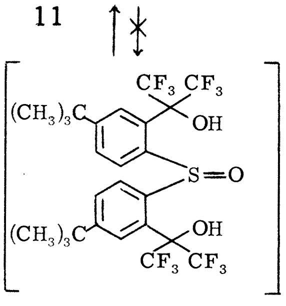
Structure and Bonding

The bonding in these species has been termed hypervalent by Musher (*1*). A qualitatively satisfactory model for the bonding in sulfuranes (*1*), like that in XeF_2 (*32*) and other hypervalent species such as ClF_3 (*33, 34*) and CH_3PF_4 (*35*), is very similar to one proposed by Pimentel (*36*) in 1951 for the symmetrically hydrogen-bonded bifluoride ion, $(F\text{-}H\text{-}F)^-$. In the present context the bifluoride ion can be viewed as a hypervalent hydrogen species. An approximate molecular orbital model for the three-center four-electron bond joining the two apical oxygens to sulfur puts the four electrons into the two lower energy molecular orbitals made up of linear combinations of *p*-orbitals on sulfur and oxygen (Fig. 1) (*33, 36*).

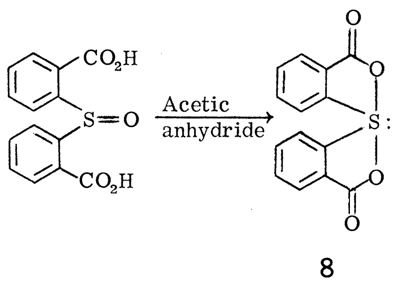
Since the two electrons in the approximately nonbonding molecular orbital are associated with the apical oxygen atoms, this model rationalizes the preference for apical positions which is seen (*13*) for more



11



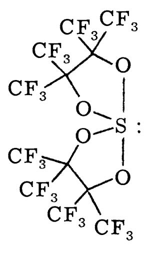
12



8

$(PhO)_4S$

9



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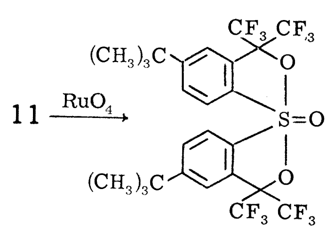
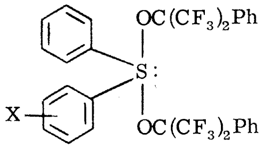


13

Structures 8-13

electronegative substituents. The net positive charge on sulfur predicted by the model is reflected in the ^{19}F chemical shifts of **14a** and **14b** (*37*).



14a (X = p-F)
14b (X = m-F)

From the ^{19}F chemical shifts, the method of Taft and co-workers (*38*) can be used to calculate resonance and inductive substituent constants for the phenyldialkoxysulfuranyl substituent, PhS$(OR_F)_2$. The value of the inductive constant (σ_I) is 0.40, indicating an electron-withdrawing inductive effect of this sulfuranyl substituent intermediate between that of the phenylsulfenyl (-SPh, 0.21) and the cationic phenylalkoxysulfonium substituent ($+S(OR_F)Ph$, -1.31), which bears a full formal positive charge on sulfur. Values of σ_I for the phenylsulfinyl (PhSO, 0.51) and the phenylsulfonyl ($PhSO_2$, 0.52) groups are very similar to that of the sulfuranyl substituent. The withdrawal of electrons by resonance reflected in a σ_R (resonance constant) value of 0.09 for the sulfuranyl substituent is intermediate between that for the PhSO-substituent (-0.01) and the Ph_2SO_2 substituent (0.14), considerably smaller than σ_R for the $+S(OR_F)Ph$ substituent (0.31).

This model of a three-center four-electron bond joining two oxygen atoms to sulfur, with two bonding and two approximately nonbonding electrons, predicts a bond order of about one-half for the apical S-O bonds. This is reflected in an increased bond length over the sum of the covalent single-bond radii (*39*) as determined by x-ray crystallography for the apical S-O bonds of **7** (elongated by 0.21 Å) (*40*) and **11** (0.13 Å) (*41*). Using the Pauling (*42*) correlation between bond order and bond length, we find that these bond elongations correspond to an S-O bond order of 0.46 for **7** and 0.62 for **11**. Table 1 summarizes important structural data for sulfuranes.

Theoretical calculations (*43*) have suggested that *d*-orbitals and higher *s*-orbitals do not make energetically significant contributions to the wave functions describing hypervalent species. Nuclear quadrupole coupling (*44*) and Mössbauer spectroscopy (*45*) of halogen analogs of the sulfuranes and photoelectron spectroscopy of SF_4 (*46*) provide experimental justification for an approximate bonding picture that describes the three-center four-electron bond without invoking *d*-orbital character.

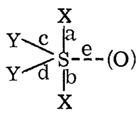
All of the sulfuranes show distorted trigonal bipyramidal (TBP) geometry with apical X-S-X angles within 8° of colinearity. The largest distortion from ideal TBP geometry is in the equatorial plane where C-S-C angles considerably less than 120° are found (a range from 101.5° to 108.1° for the sulfuranes).

The sulfurane oxides, in which an oxygen ligand replaces the sulfurane lone pair, are more nearly regular TBP molecules (**13** shows a C-S-C angle of 117.7°) (*41*). The equatorial S=O bond of **13** has a length nearly identical to that found for the S=O bonds in sulfones (*47*). The similarity to the sulfone S=O bond is also seen in the low basicity of **13**, in marked contrast to the basicity of the oxygen of sulfoxides (*48*). No evidence of reaction of **13** with acids was seen (*31*) in a variety of experiments involving sensitive probes for such reactions, even with very strong acids.

A sensitive stereochemical probe is available in ^{19}F nuclear magnetic resonance (NMR) spectroscopy of sulfuranes containing suitable structural features. The CF_3 groups of **11** are nonequivalent (*cis* and *trans* to aryl) and show up as two quartets (J_{FF} = 9 hertz, where J is the spin-spin coupling constant); at 73.9 and 77.0 ppm upfield from $CFCl_3$. This spectrum was essentially unchanged up to 200°C, setting a lower limit to the free energy of activation ΔG^* for the inversion process, which would interchange exo and endo CF_3 groups, of $>$ 25 kcal/mole (*41*). This is at least comparable to the value (25 to 29 kcal/mole) (*49*) for the barrier to pyramidal inversion reported for sulfonium ions. The conformation with four coplanar bonds to sulfur is therefore a high energy one.

When the four groups attached to sulfur are identical, as in tetraarylsulfurane **6** (*21*) or spirotetraalkoxysulfurane **10** (*30*), published NMR evidence has usually failed to provide evidence for nonequivalence of apical and equatorial ligands. While SF_4 shows nonequivalent fluorine atoms at very low temperatures, considerable ambiguity has existed as to whether the exchange responsible for the coalescence seen for the peaks of higher temperatures was intermolecular or intramolecular (*50*). The NMR of **10** is of particular interest in that at room temperature (*30*) two equivalent ^{19}F multiplets are observed consistent with either the square pyramidal geometry of **10b**, which contains only two kinds of CF_3 group, or with a rapidly equilibrating mixture of distorted TBP structures **10a** and **10c**, interconverted by the Berry (*51, 52*) pseudorotation process. We have shown (*53*) by ^{19}F NMR studies at temperatures down to -150°C that the TBP structures are favored, with clear evidence for four nonequivalent CF_3 groups. The barrier for pseudorotation is low ($\Delta G^*_{-100°C}$ = about 7.5 kcal/mole) and that for inversion through

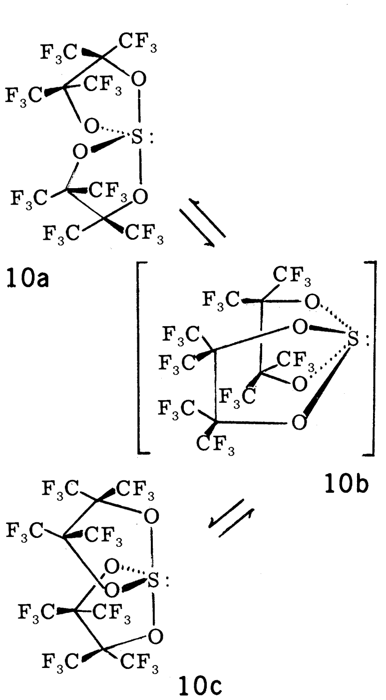
Table 1. A comparison of bond lengths and bond angles about sulfur in sulfuranes and sulfurane oxides.



	X = OR, Y = aryl				X = Cl, Y = aryl		X = Y = F		
	11 (*41*)	**11***	**13** (*41*)	**7** (*40*)	**8** (*28*)	$(p\text{-}ClC_6H_4)_2SCl_2$ (*16*)	**1** †	**1** ‡	SOF_4§
Bond a (Å)	1.819	1.816	1.777	1.916	1.83	2.259	1.643	1.646	1.575
Bond b (Å)	1.832	1.831	1.780	1.889	1.83	2.323	1.643	1.646	1.575
Bond c (Å)	1.803	1.803	1.796	1.810	1.82	1.797	1.542	1.545	1.552
Bond d (Å)	1.787	1.798	1.784	1.803	1.82	1.767	1.542	1.545	1.552
Bond e (Å)			1.439						1.403
∠ ab (deg) ǁ	182.9	181.8	187.7	184.9	181.5	174.5	183.2	186.9	181.3
∠ cd (deg)	198.1	107.6	117.7	104.4	107.8	108.6	103.8	101.5	110.1
∠ ae (deg)			94.3						90.6
∠ be (deg)			93.4						90.6

*Second independent molecule of **11** in unit cell. †Electron diffraction study (*12*). ‡Microwave study (*11*). §Electron diffraction study (*12*). For other electron diffraction studies see (*70*). ǁIn this table the angle *ab* is defined as including either the equatorial oxygen atom or the sulfur lone pair of electrons.

a planar geometry is again above 25 kcal/mole, as evidenced by the lack of change in the room temperature spectrum upon going to 200°C.


10a

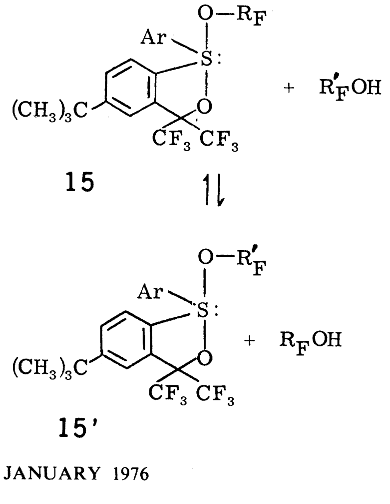
10b

10c

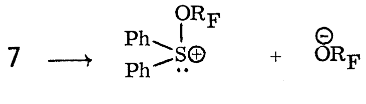
Five-Membered Ring Effect

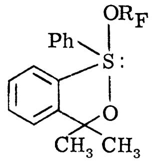
The stabilization of TBP compounds of hypervalent phosphorus (phosphoranes), relative to the corresponding four-coordinate tetrahedral phosphorus(V) species such as phosphate esters, by the bridging of an apical and an equatorial position with a five-membered ring has been well documented (*48, 54*). The large (factors up to 10^7) effects of the ring on equilibrium and rate constants have been generally attributed to ring strain effects (*52, 54, 55*).

The effect is also very important in sulfuranes. For example, the pictured degenerate ligand exchange for **15**, which can be followed by ^{19}F NMR lineshape analysis, is only 10^{-4} as fast as the analogous reaction of acyclic sulfurane **7**. Since the ligand exchange reactions of **7** have been shown (*37*) to proceed by ionization to the alkoxysulfonium cation **16**, which can be considered to be a distorted tetrahedral molecule, it is clear that the five-membered ring of **15** is slowing this ionization, which converts TBP to tetrahedral geometry, by a factor of at least 10^4 (*31*). The ionization in **15** is also slowed by inductive electron-withdrawal by the CF_3 substituents since **17**, despite its five-membered ring, undergoes the degenerate ligand exchange with R_FOH more rapidly than does **15** by a factor of more than 10^4, almost the same as the rate seen for **7**. The five-membered ring effect is less important in determining the rate of ionization than is the substituent change on going from **7** to **17**.

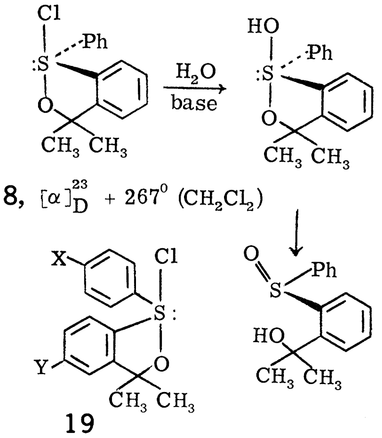

15

15'


16


17

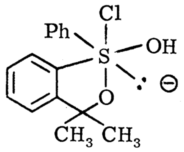
Optically active chlorosulfurane **18** has been prepared in 96 percent enantiomeric purity (*56*). The covalent nature of the S-Cl bond is evidenced in the appearance of a molecular ion in the field desorption mass spectrum of **18** and by several lines of evidence from ^{1}H and ^{13}C NMR studies. The base catalyzed hydrolysis of **18** proceeds with retention of configuration at sulfur.



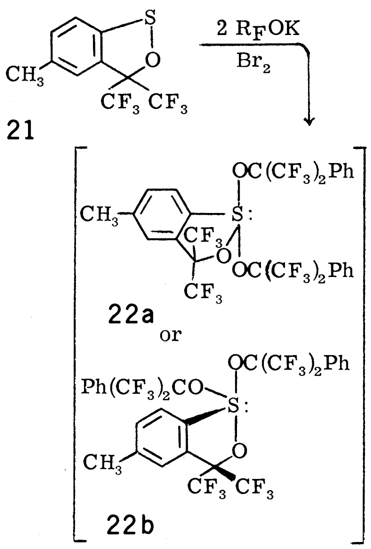
18, $[\alpha]^{23}_{D}$ + 267° (CH_2Cl_2)

19

Rates for the hydrolysis of analogs of **18** substituted in both aromatic rings (**19**, X = Y = H; X = Y = CH_3; X = Cl, Y = H; X = H, Y = Cl; X = NO_2, Y = H; and X = H, Y = NO_2) were accelerated by electron-withdrawing substituents (ρ_X = 0.3, ρ_Y = 2.0), where ρ is the reaction constant in the Hammett equation (*56a*), suggesting a reaction with hydroxide in an associative reaction via transition state (or intermediate) **20** or one of its stereoisomers.


20

Although the racemization of **18** is rapid in the presence of HCl, it is configurationally stable when an organic base is added to scavenge the HCl. Racemization by inversion (through the planar geometry) or by pseudorotation pathways must have a free energy of activation greater than 25 kcal/mole. The pseudorotation pathways for inversion, unlike those for phosphorane inversion (*57*), involve intermediate states that approximate TBP conformations with apical lone pairs. In our approximate molecular orbital bonding scheme this is equivalent to breaking the other apical bond, and the slowness of racemization is consistent with the idea that these are indeed high energy conformations.



21

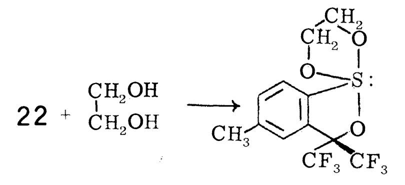
22a

or

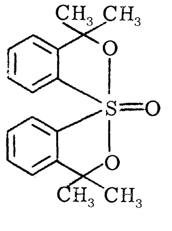
22b

Trialkoxysulfurane **22**, prepared in the usual way from the divalent sulfur precursor (*58*) sultene **21**, is interesting in that two conformations are possible, each of which has two apical alkoxy ligands. They differ in that one, **22a**, has the five-membered ring bridging two equatorial positions while the other, **22b**, has the more usual apical-equatorial bridge. The equivalence in ^{19}F NMR of the two CF_3 groups on the five-membered ring, even at -90°C, strongly favors structure **22a** for this compound. While compound **4** has a four-membered ring bridging equatorial rings, the conformation could be forced into that pictured by the great apicophilicity of the electronegative fluorine ligands of **4**. The preference for apical-equatorial bridging in phosphorane analogs of **22** is well known (*52, 54, 59*). The apparent preference for conformation **22a** probably reflects the smaller angle between equatorial ligands seen for sulfuranes compared to the near 120° normal for such angles in unstrained phosphoranes.

Treatment of **22** with ethylene glycol gives, in a reaction found (*58*) to be typical for many bifunctional ligands, rapid formation of stable spirosulfurane **23**. The spiro structure forces both rings into apical-equatorial bridging, and this is reflected in nonequivalence of the CF_3 groups in the NMR spectrum of **23**.


23

The remarkable influence of five-membered rings on sulfurane stability has been exploited to make available a large number of novel compounds stable enough to allow isolation or spectroscopic examination in solution (*60*). Among these are compounds **24** to **29**. (The compound assigned structure **28** may be the isomeric sulfurane with S-O, rather than S-N bonds.)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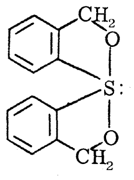
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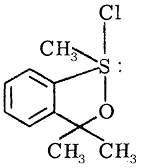
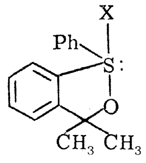
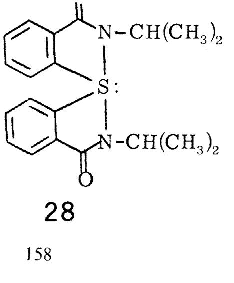
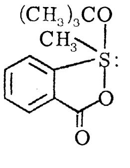

26


27a (X = Cl)
27b (X = OPh)
27c (X = CN)
27d (X = N_3)
27e (X = $OCOCH_3$)


28

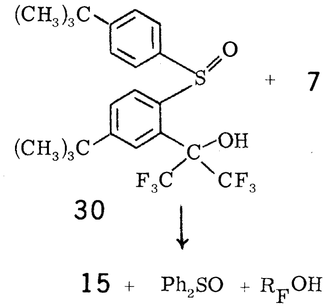

29

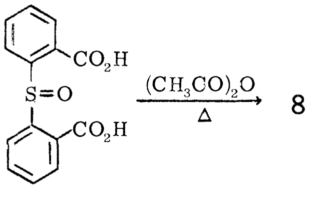
Synthetic Methods

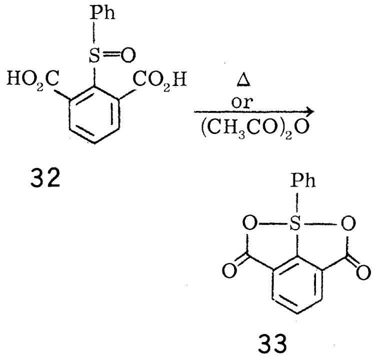
Oxysulfuranes are accessible via a number of synthetic procedures. In addition to the previously mentioned chlorine or bromine oxidation of a sulfide (*23, 37*) or sulfenate (*58*) in the presence of R_FOK, the reaction of sulfonium triflates, $[ROS^+Ph_2][CF_3SO_2O^-]$, with R_FO^- also gives oxysulfuranes (*60*). This is a convenient route to the sulfuranes since the acyclic sulfoxide alcohols, for example, **30**, may be cyclized by the addition of 2 moles of triflic acid, CF_3SO_3H.

Acyclic sulfurane **7**, a powerful dehydrating reagent, has been shown to react (*31*) with sulfoxide alcohols, for example, **30**, to form cyclic oxysulfuranes, for example, **15**.

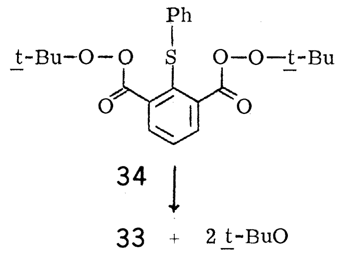
Dehydration leading to sulfuranes from their acyclic sulfoxide precursors is favored by the production of a five-membered ring. We have already mentioned the rapid and complete conversion of **12** to **11** by cyclodehydration. Kapovits and Kálmán (*28*) reported that **31** is converted into **8** by sublimation or by treatment with acetic anhydride. Similar reactions convert diacid **32** to **33** in high yields (*61*). The second pictured route to **33**, by thermolysis of diperester **34**, has been shown to proceed by a fascinating new mechanism (*61*) involving simultaneous formation of two S-O bonds as the two O-O bonds are broken via a transition state resembling **35**.

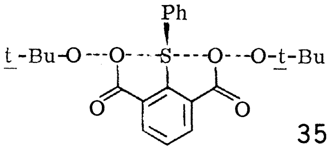

30

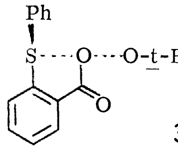

31


32

33

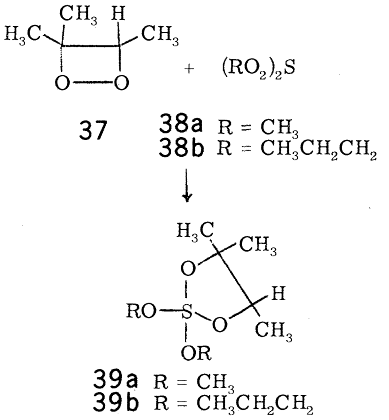

34


35


36

Simultaneous kinetic participation of three neighboring groups is reflected in the anchimeric acceleration of radical formation via **35** (a factor of about 10^7 at 0°C). That this factor is substantially greater than the acceleration of the decomposition of the corresponding monoperester via **36** (a factor of about 10^5 at 0°C) is a manifestation of substantial hypervalent bonding in transition state **35**. We are tempted to term the greater degree of participation of sulfur when flanked by two perester functions as in **34** the "Samson effect" (*62*).

A related reaction of a peroxide with a sulfur(II) species to yield a sulfurane is reported by Denney (*63*) to occur when a dioxetane (**37**) is treated with a sulfoxylate (**38**) to give a tetraoxysulfurane (**39**), an orthosulfite (*64*) which is thermally decomposed on warming from -78°C.


37

38a R = CH_3
38b R = $CH_3CH_2CH_2$

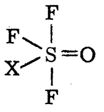
39a R = CH_3
39b R = $CH_3CH_2CH_2$

The first known orthosulfite was the perfluoropinacol derivative **10**. This was prepared (*30*) by the action of disodium perfluoropinacolate on sulfur dichloride. Phenyl orthosulfite, **9**, a white hygroscopic solid hydrolyzed to phenol and diphenyl sulfite, was prepared (*29*) by reaction of 4 moles of phenoxytrimethylsilane with SF_4.

Several routes have been used in the formation of halosulfuranes. Oxidations of sulfur(II) species by fluorinating agents such as CoF_3 (*7*), AgF_2 (*9*), or CF_3OF (*17*) to give fluorosulfuranes have been supplemented by reactions involving the replacement of the fluorine substituents of SF_4 with other groups (*21*). Middleton (*65*) prepared aminosulfurane **41** by the reaction of SF_4 with trimethylsilylamine **40**.

$$\begin{array}{ccc} SF_4 & & FSi(CH_3)_3 \\ + & \longrightarrow & + \\ (CH_3)_2NSi(CH_3)_3 & & (CH_3)_2NSF_3 \\ \mathbf{40} & & \mathbf{41} \end{array}$$

Fluorosulfurane oxides, SF_4O and its derivatives, have been prepared by the fluorination of SOF_2 (*66*) or perfluoroalkyl sulfoxides (*67*) with F_2 or by the oxidation of SF_4 with nitrogen oxides or oxygen in the presence of NO_2 at high temperatures (*68*). Sulfurane oxide **13** was prepared (*31*) by the RuO_4 oxidation of **11** while sulfurane oxide **24** was prepared by the ozonolysis of the corresponding sulfurane (*60*). The replacement of fluorines of SF_4O with other substituents by treatment with a suitable silane ($XSiMe_3$) has been reported (*69*) to lead to compounds of type **42**.



($X = CH_3, C_2H_5, C_6H_5O$)

42

Summary

The development of synthetic methods for oxysulfuranes has made a wide range of isolable compounds of hypervalent sulfur available for study. Structure-reactivity correlations are now becoming evident as a result of such study. The fact that oxygen is dicoordinate makes it possible to synthesize cyclic oxysulfuranes and to use the pronounced changes of reactivity which accompany cyclization to design new, potentially useful sulfurane reagents stable enough to allow isolation.

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