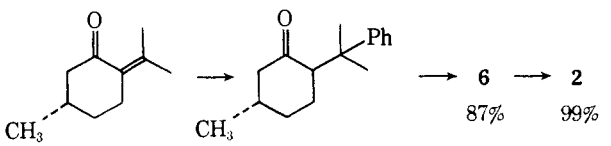
thyl acrylate.[2b] The addition of the enolate of **3** (1.1 equiv of lithium diisopropylamide, −78 to 0° for 1 hr) to an oxygenated solution of THF at −78° containing 2 equiv of triethylphosphite[6] produced the α-hydroxy esters (**4**) as an oil (ca. 2:1 mixture of exo- and endo-hydroxyl). The hydroxy esters (**4**) were directly reduced with excess lithium aluminum hydride to a mixture of endo and exo diols (**5**) and the alcohol (**6**). Filtration of the crude reaction mixture through a tenfold amount of silica gel gave the optically pure alcohol (**6**) (eluted with benzene:ether, 20:1) as an oil, $[\alpha]^{23}D$ +26.3° (*c* 2.02, EtOH), and a mixture of endo- and exo-diols (**5**) (eluted with ether:ethanol, 20:1) as an oil. Since **6** is recovered pure and in high yield, it can efficiently be recycled. Treatment of **5** with 1.4 equiv of sodium metaperiodate in aqueous *tert*-butyl alcohol (buffered to pH 7) gave the optically active ketone **7** as an oil, $[\alpha]^{23}D$ −365° (*c* 1.29, $CHCl_3$).[7,8]

The ketone **5** was converted to the known, optically active iodolactone[1d] by treatment with basic hydrogen peroxide[9] to give the acid-sensitive hydroxy acid which was treated with 2.5 equiv of potassium triiodide in aqueous sodium bicarbonate (24 hr, 0°) to give optically pure **1**, mp 120–121° (from methylene chloride–hexane), $[\alpha]^{23}D$ −33.3° (*c* 1.3, $CHCl_3$),[10] 89% yield from **7**.

The optically pure acrylate (**2**) was prepared in 71% yield from optically pure (−)-pulegone.



8

85%

S-(−)-Pulegone was treated with 1.2 equiv of phenylmagnesium bromide in the presence of cuprous chloride to give a kinetic mixture (ca. 1:1) of cis and trans ketones (**8**). Equilibration with ethanolic potassium hydroxide gave the expected[11] 85:15 mixture which was directly reduced with sodium–isopropyl alcohol in refluxing toluene.[12] Since the more stable *trans*-**8** is reduced to the equatorial alcohol more rapidly than *cis*-**8**, equilibration occurs, and one obtains almost entirely the all equatorial alcohol (**6**).[13] The acrylate (**2**) was prepared by treatment of **6** with 1.5 equiv of triethylamine and 1.2 equiv of acryloyl chloride.

The (−)-pulegone used was prepared by treatment of (−)-citronellol,[14] $[\alpha]^{20}D$ −4.1° (neat), with 2.5 equiv of pyridinium chlorochromate[15] in dry methylene chloride for 40 hr.[16] Treatment of the isopulegone with ethanolic potassium hydroxide and distillation gave a 70% yield of *S*-(−)-pulegone, $[\alpha]^{20}D$ −20° (neat).[17]

Optically pure (−)-pulegone was prepared by recrystallization of its semicarbazone from ethanol. Treatment of the fully resolved semicarbazone, mp 170–171° (recrystallized three times from ethanol), $[\alpha]^{22}D$ −65.23°[18] (*c* 2.2, $CHCl_3$), with excess pyruvic acid in glacial acetic acid gave *S*-(−)-pulegone, bp 104–106° (22 mm), $[\alpha]^{23}D$ −22.5°.[19]

The chiral alcohol **6** (or, equivalently, its enantiomer (−)-**6**, prepared from (+)-pulegone) is dramatically superior to (−)-menthol in chiral directing ability. For example, Hamer[2a] reports the stannic chloride catalyzed Diels–Alder reaction of (−)-menthyl acrylate with cyclopentadiene at 4° in toluene gave, after lithium aluminum hydride reduction and vapor phase chromatography, *endo*-bicyclo[2.2.1]hept-2-enecarbinol, $[\alpha]^{25}D$ +31.4° (ethanol).[20] Under identical conditions (+)-*endo*-bicyclo[2.2.1]hept-2-enecarbinol, $[\alpha]^{22}D$ +76.1° (*c* 0.9, ethanol), was obtained from the reaction of (−)-**2** with cyclopentadiene.[21,22]

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(3) Higher temperatures cause total polymerization of the diene.

(4) A small amount (ca. 7%) of the exo adduct is formed. No evidence for other isomers of **3** was found.

(5) Satisfactory NMR, ir, and high resolution mass spectra were obtained for all compounds reported herein.

(6) This in situ formation and reduction of the α-hydroperoxy ester was found to be superior to other methods. See D. S. Watt and S. J. Selikson, *J. Org. Chem.*, **40**, 267 (1975); H. H. Wasserman and B. H. Lipshutz, *Tetrahedron Lett.*, 1731 (1975).

(7) The ORD curve of **7** is similar to that of other β,γ-unsaturated ketones. $(\phi)_{3190}$ = −22300°, $(\phi)_{3010}$ = 0°, $(\phi)_{2790}$ = +20100° (*c* 0.0342, EtOH). See K. Mislow and J. G. Berger, *J. Am. Chem. Soc.*, **84**, 1945 (1962); A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *ibid.*, **84**, 1956 (1962).

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(10) Lit.[1d] mp 120–122°, $[\alpha]^{25}D$ −34.0° (*c* 1.1, $CHCl_3$); prepared by resolution of the precursor unsaturated acid as the (+)-amphetamine salt.

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(17) The conversion of citronellol to pulegone using "conventional" reagents (i.e., (1) $CrO_3 \cdot 2C_5H_5N$; (2) *p*-TsOH, CH_2Cl_2; (3) Jones oxidation; (4) EtOH–KOH) gave pulegone in much lower yield.

(18) Lit. mp 171–172°, $[\alpha]^{20}D$ +61.7° (*c* 4.0, $CHCl_3$) for semicarbazone of (+)-pulegone: Y. Naves and P. Ochsner, *Helv. Chim. Acta*, **47**, 51 (1964). In our hands, mp 170–171°, $[\alpha]^{23}D$ +66° (*c* 2.05, $CHCl_3$).

(19) Lit. bp 81° (5 mm), $[\alpha]^{22}D$ +23.56°: W. J. Houlihan, *J. Org. Chem.*, **27**, 4096 (1962).

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(21) We are grateful to Dr. Jasjit S. Bindra (Chas. Pfizer and Co.) for encouraging us to undertake this project and for helpful suggestions and discussions.

(22) This investigation was assisted financially by the National Science Foundation.

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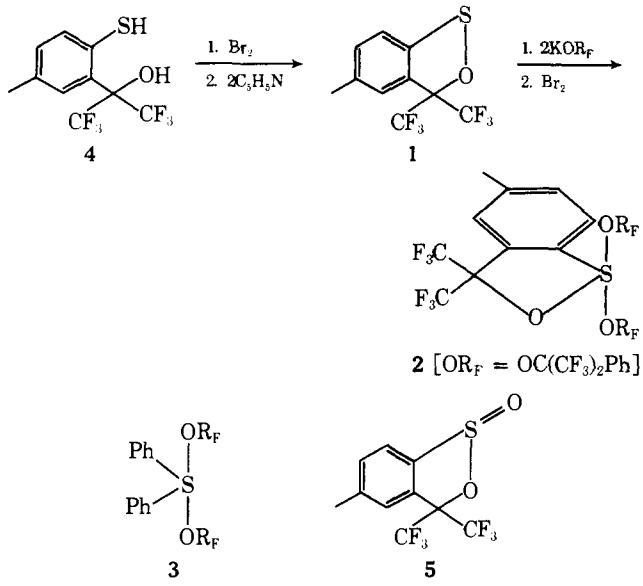
Received July 25, 1975

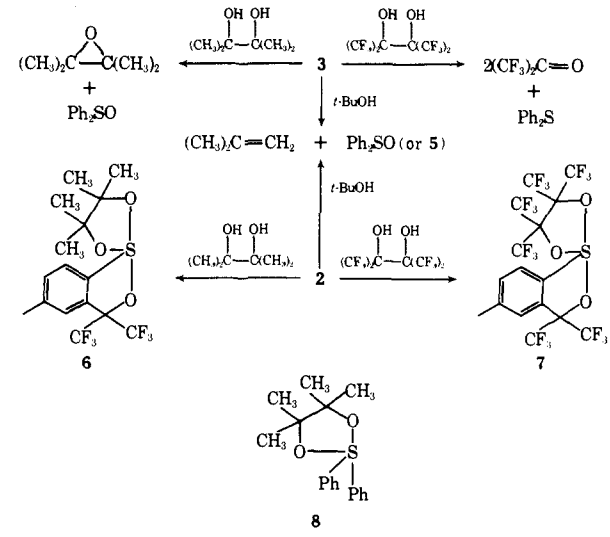
An Aryltrialkoxysulfurane Prepared from a Cyclic Sulfenate. Polarity Rules and Sulfurane Reactivity[1]

Sir:

We report the synthesis of the first cyclic sulfenate, sultene **1**, and its conversion to aryltrialkoxysulfurane **2**, which appears to exist in a conformation with a five-membered diequatorial ring. This sulfurane, in contrast to well-studied diaryldialkoxysulfurane **3**,[2f-h] reacts with several bifunctional alcohols to give stable spirosulfuranes with five and six-membered rings.

No sultenes have ever been reported, although cyclic sulfenates have been proposed as reactive intermediates[3] and suggested to explain mass spectral fragmentation.[4] Sultene **1** is prepared in 85% yield in CCl_4 by the reaction of **4** with bromine and pyridine at −5°. Recrystallization from pen-





tane gives yellow crystals (mp 49–50.5°)[5] which are stable indefinitely at room temperature.[6]

Since the sulfenate reacts within minutes at room temperature with water or moist air to give sulfinate **5** and other products, it must be handled in a dry atmosphere. It also reacts slowly (5 days at 25° in CCl_4 solution) with *tert*-butyl perbenzoate to give sulfinate **5** and isobutylene, identified by their ^1H and ^{19}F NMR spectra.[7] A possible mechanism for this reaction would involve sulfur insertion into the peroxide bond to give a sulfurane intermediate. Analogous biphilic insertions to give hypervalent compounds are well known in phosphorus chemistry[8] and have recently been reported for the reaction of dioxetanes with a sulfoxylate.[9]

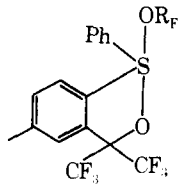
The high reactivity of **1** may reflect lone pair repulsion between sulfur and oxygen nonbonding electrons in the nearly planar five-membered ring. Similar observations have been made for sulfenamides,[10] peroxides,[11] and disulfides.[12] The bathochromic shift in the electronic spectrum of **2** (383 vs. 277 nm for an acyclic sulfenate[13]) parallels that noted for cyclic disulfides[12] and peroxides.[14]

Sulfenate **1** is converted in 43% yield by reaction with 1 equiv of bromine and 2 equiv of the potassium salt of hexafluoro-2-phenyl-2-propanol (KOR_F) to white crystalline sulfurane **2** (mp 140.5–141°),[15] the first reported aryltrialkoxysulfurane.[16]

Sulfurane **2** acts similarly to diaryldialkoxysulfurane **3**[2e-g] in that it dehydrates *tert*-butyl alcohol to give isobutylene very rapidly at room temperature. In reactions with bifunctional compounds, however, the parallel between **2** and **3** breaks down. Pinacol reacts with **3** to give epoxide[2f] but reacts with **2** to give 63% of spirosulfurane **6**, mp 108–109.5°.[20] Perfluoropinacol is oxidatively cleaved by **3**, but forms spirosulfurane **7** upon treatment with **2**. This difference in reaction pathways for sulfuranes **2** and **3** is not surprising since the formation of a cyclic product from **3** (compound **8**) would violate electronegativity rules[21,22] by requiring a phenyl to occupy an apical position.

Evidence that this route to spirosulfuranes is general is seen in reactions of **2** with a number of other bifunctional compounds including ethylene glycol, perfluoropinacol, and 2,2-dimethyl-1,3-propanediol. In each case evidence for spirosulfurane formation was seen in the diastereotopic nature of substituents (methylene hydrogens, CH_3 groups, or CF_3 groups) of the bifunctional ligand. Also seen is a low field ^1H NMR doublet highly characteristic for the proton ortho to sulfur in an apical-equatorial bridged arylsulfurane such as **6** or **7**. (Many analogues of **6** and **7** have been studied[1,2b] and x-ray structures have established, for two of these,[2d,j] the trigonal bipyramidal geometry which we have assumed in this paper.) The product formed from 2,2-dimethyl-1,3-propanediol is noteworthy as the first sulfurane with a six-membered ring.

R_FOH–ether solutions of **2** showed extensive broadening of the hexafluorocumyl quartets in the ^{19}F NMR at 41° when 50–60% R_FOH by volume was present. This indicates a much slower rate of degenerate ligand exchange for **2** than for **9**[2b] or **3**.[2h] This ligand exchange has been shown



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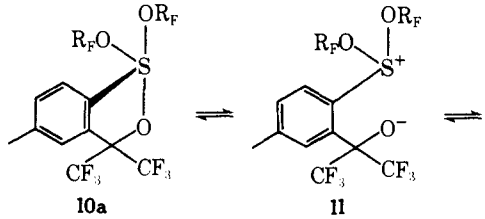
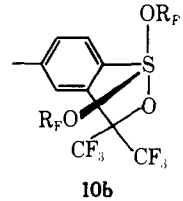
for acyclic sulfurane **3** to proceed by ionization to give the alkoxysulfonium ion.[2e,h,i] We would therefore attribute the slower exchange of **2** with R_FOH to a destabilizing inductive effect of the equatorial alkoxy substituent on the transition state for ionization. Support for this mechanistic view comes from the observed broadening of the OR_F quartets by the addition of small amounts of a more acidic alcohol, perfluoro-*tert*-butyl alcohol.

Since two covalent structures **2** and **10** satisfy both the



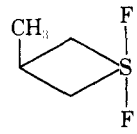
10a 11



10b

electronegativity rules[21,22] and the restriction against diapical linkage of five-membered rings, this compound presents a rare opportunity to study the relative importance of steric and ring strain effects[22] in determining conformations of sulfuranes. The ^{19}F NMR of **2** (which shows equivalent CF_3 groups on the ring) is compatible with diequatorial structure **2** or with a rapid equilibrium between **10a** and **10b.** The latter is considered highly unlikely since no peak broadening is seen in the 94.1-MHz ^{19}F NMR spectrum, even at −90°. Neither was the low-field aromatic ^1H NMR doublet, previously mentioned as being highly characteristic of an apical-equatorial bridged arylsulfurane, present in the NMR, although it would be expected for structures **10a** or **10b.** We also reject the zwitterionic structure **11** on the basis of the solubility of **2** in nonpolar solvents such as CCl_4 and upon the basis of analogies with other sulfuranes for which x-ray structures are available.[2c,d,j]

The apparent preference for the diequatorial five-membered ring fusion in **2** is at first glance surprising, in view of contrasting experience in phosphorane chemistry. Although a few structures are known in which four- and six-membered rings link equatorial positions of phosphoranes,[22b,23] these are all cases in which the great difference in apicophilicities pushes two fluoro or alkoxy ligands into the apical position with the two less electronegative carbon ligands of the ring being forced into the diequatorial geometry. A similar difference in apicophilicity would tend to favor the diequatorial disposition of the four-membered ring in sulfurane **12.**[24]



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The preference for the diequatorial linkage in sulfurane **2** can be rationalized by reference to the smaller bond angles in the equatorial plane which have been reported for sulfuranes[2c,d,j,25] (104.4–108.1°) relative to the near 120° of the three bond angles in the equatorial plane of phosphorane analogues.[26] It is less clear why a recently prepared monocyclic tetrakisalkoxysulfurane should have an equatorial-apical five-membered ring.[9]

Acknowledgment. This research was supported in part by a grant from the National Science Foundation (MPS 71-03222) and in part by Fellowships for G.W.A. from Abbott Laboratories, the Phillips Petroleum Co., and the Dow Chemical Co.

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(6) The thermal stability is in marked contrast to that evidenced by an analogous cyclic sulfenyl carboxylate for which L. Field, P. M. Giles, Jr., and D. L. Tuleen, *J. Org. Chem.*, **36**, 623 (1971), report noticeable polymerization to occur in 0.5 hr at 25°.
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(15) Anal. Calcd for $C_{26}F_{18}H_{16}SO_3$: C, 43.42; H, 2.08. Found C, 42.75; H, 2.26 (the analysis was difficult because of the extreme water sensitivity of **2**). ^1H NMR (CCl_4) δ 2.63 (s, 3, CH_3), 7.28 (broad s, 10, hexafluorocumyl groups), 7.61 (broad s, 3, trisubstituted ring); ^{19}F NMR (CCl_4) broad quartets, 70.1 and 72.7 ppm upfield from $CFCl_3$ (broad q, 6 each, CF_3 groups of OR_F), 71.4 ppm (broad s, 6, ring CF_3); mass spectrum (70 eV) *m/e* (rel intensity) 705 (0.02, M − CF_3), 697 (0.01, M − Ph), 531 (15.5, M − OR_F), 227 (100, $PhC(CF_3)_2$+), field ionization mass spectrum *m/e* (rel intensity) 774 (0.1, $M^{\cdot+}$), 551 (0.2), 532 (100, M + H − OR_F).
(16) Thermally unstable trichlorosulfuranes[17] and highly reactive trifluorosulfuranes[18] are well known. One fluorotrialkoxysulfurane has also been reported.[19]
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(20) ^1H NMR (C_6D_6) δ 0.78 (s, 3, CH_3), 0.86 (s, 3, CH_3), 0.98 (s, 3, CH_3), 1.07 (s, 3, CH_3), 1.86 (s, 3, $ArCH_3$), 6.87 (broad d, 1, proton para to fluoroalkyl group, J = 8 Hz), 7.6 (broad s, 1, proton ortho to fluoroalkyl group), 8.13 (d, 1, proton ortho to sulfur); ^{19}F NMR (CCl_4) 2 quartets 75.35 and 76.23 ppm upfield from $CFCl_3$, J = 9 Hz; mass spectrum (70 eV) *m/e* (rel intensity) 405 (0.3, M + H), 389 (2.06, M − CH_3), 335 (1.95, M − CF_3), 219 (100).
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New Synthetic Reactions. New Approach to (Alkylative) Oxidative Ring Cleavage

Sir:

The utility of cyclic compounds for control of stereochemistry in organic synthesis as well as, to a lesser extent, the modification of ring size depends upon the ability to selectively cleave rings. Methods which involve generation of vicinal oxygen substitution (e.g., by oxidation of an olefin or ketone) are common.[1-4] The selective sulfenylation of polyfunctional compounds[5,6] suggests the desirability of replacing oxygen substituents with thio groups in many oxidative processes.[7]