synthesized by cyclodehydration, a process of stepwise ketalization of 8-S-4 species (sulfones) to 10-S-5 species (sulfurane oxides) and then to 12-S-6 species (persulfuranes). The second step in this sequence has already been observed to occur.[13]

Acknowledgment. The research was supported in part by a grant from the National Science Foundation (CHE-7905692). We also acknowledge the assistance of Dr. Eileen N. Duesler, who obtained the X-ray structure.

Registry No. 1, 32133-82-7; 2, 33973-62-5; 6, 78479-63-7; 7, 78479-64-8; 8, 75894-03-0; 9, 75893-96-8; 10, 78479-65-9; 11, 75893-98-0; 12, 75893-89-9; 13, 78479-66-0; 15a, 75893-97-9; 17a, 78479-67-1; 18, 78479-68-2; 19, 78479-69-3; 20, 78479-70-6.

Supplementary Material Available: Listings of the atomic coordinates (Table I), the thermal parameters (Table III), and bond angles and lengths (Tables IV and V) (9 pages). Ordering information is given on any current masthead page.

Apical Ligand Preference and Fluxional Behavior of Some Sulfuranes

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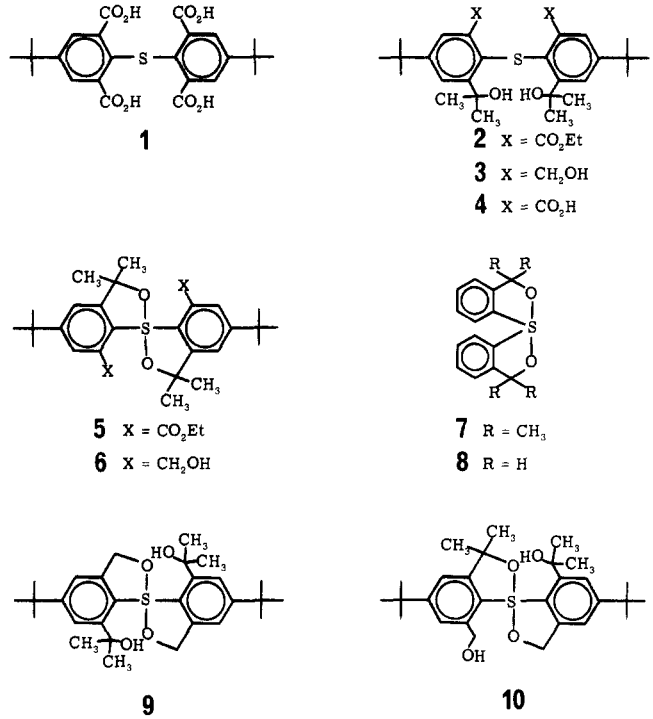
Sulfides **4**, **11**, and **12** react with *m*-chloroperbenzoic acid to form apically unsymmetrically substituted sulfuranes **18–20**, respectively, instead of the isomeric symmetrically substituted dialkoxysulfuranes. Rapid equilibration ($\Delta G^*_{12°C}$ = 14.7 kcal mol^{-1}) of isomers of sulfurane **18** is observed and studied by ^{1}H NMR spectroscopy. An associative mechanism for these interconversion processes is proposed. Potassium salts of **18** and **19** are symmetrical dialkoxysulfuranes **21** and **22**, respectively. Other reactions involving these sulfuranes are also reported.

In the course of our studies on persulfuranes,[1] a number of completely ortho-substituted diaryl sulfides such at **1–4** (Chart I) were synthesized. Dialkoxysulfuranes **5**[1] and **6**,[2] analogues of sulfurane **7**,[3] were prepared from sulfides **2** and **3**, respectively. It is interesting that no evidence is found, in the case of **6**, for the presence of isomeric symmetrical sulfurane **9** or unsymmetrical sulfurane **10**, even though sulfurane **8**, a close analogue of **9**, has been synthesized[3] and found to be stable at room temperature. Structure **6** with apical tertiary alkoxy ligands is therefore preferred over **9** with its two primary alkoxy ligands and the unsymmetrical isomer **10**. No evidence was seen for intramolecular ligand exchanges between the primary and tertiary alcohol substituents. We report here the conformational preference and fluxional behavior of the sulfurane formed by oxidation from sulfide **4** and related observations on the reactions of other sulfuranes.

Chart I



Experimental Section

General Methods. Proton chemical shifts are reported on the δ scale (parts per million downfield from tetramethylsilane as an internal standard). Melting points were determined on a micro hot stage. Elemental analyses of new compounds are within 0.4% of the theoretical values unless otherwise noted.

Solvents and Reagents. Ether, tetrahydrofuran (THF), and pentane were dried and stored over sodium wire. Chloroform and methylene chloride were washed with concentrated H_2SO_4, water, and then 10% $NaHCO_3$ before being distilled from P_2O_5.

7-(1-Hydroxy-1-methylethyl)-7′-carboxy-5,5′-bis(1,1-dimethylethyl)-3-oxo-3′,3′-dimethyl-1,1′-spirobi[3*H*-2,1-benzoxathiole] (Hydroxy Acid Sulfurane 18). A solution of *m*-chloroperbenzoic acid (1.24 g of 85% peracid, 6.1 mmol) in 40 mL of $CHCl_3$ was added in one portion to a suspension of sulfide diacid diol **4** (3 g, 5.98 mmol) in 80 mL of $CHCl_3$. After 40 min, the solution was filtered, washed with aqueous $NaHCO_3$, and dried (Na_2SO_4), and the solvent was removed to leave a solid, which was recrystallized from ether–CH_2Cl_2 to give **18**: 1.7 g (3.41 mmol, 57%); mp 181.5–182.5 °C; IR (CH_2Cl_2) 3546 (m), 1715 (br, s), 1616 (s), 1587 (s) cm^{-1}; ^{1}H 220 MHz NMR ($CDCl_3$, −30 °C) δ 8.04 (br, 1, Ar H), 7.46 (br, 1, Ar H), 7.35 (br, 1, Ar H), 7.18 (br, 1, Ar H), 6.1 (br, 2, OH), 1.93 (s, 3, $OCCH_3$), 1.84 (s, 3, $OCCH_3$), 1.80 (s, 3, $OCCH_3$), 1.65 (s, 3, $OCCH_3$), 1.41 (s, 9, $C(CH_3)_3$), 1.26 (s, 9, $C(CH_3)_3$); ^{1}H NMR (Me_2SO-d_6, 90 °C) δ 7.68 (d, 2, Ar H), 7.52 (d, 2, Ar H), 1.84 (s, 6, $OCCH_3$), 1.71 (s, 6, $OCCH_3$), 1.38 (s, 18, $C(CH_3)_3$); mass spectrum (70 eV), *m/e* (relative intensity) 500 ($M^{+\cdot}$, not observed), 482 (2.85, $M^{+\cdot} - H_2O$), 464 (100, $M^{+\cdot} - 2H_2O$), 449 (31.27, $M^{+\cdot} - 2H_2O$ and CH_3), 431 (25.47, $M^{+\cdot} - 3H_2O$ and CH_3), 405 (10.87, *m/e* 499 − CO_2). Anal. ($C_{28}H_{36}O_6S$) C, H.

Sulfurane **18** was found to be hygroscopic. Crystals of **18** may contain a molecule of water of crystallization, as observed in the

(1) (a) Lam, W. Y.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 1659. (b) *Ibid.* **1981**, *103*, 120.
(2) Lam, W. Y.; Martin, J. C. *J. Org. Chem.*, preceding paper in this issue.
(3) Adzima, L. J.; Martin, J. C. *J. Org. Chem.* **1977**, *42*, 4006.

0022-3263/81/1946-4468$01.25/0

^{1}H NMR spectrum (a total of four OH protons are sometimes seen). Anal. ($C_{28}H_{36}O_6S\cdot H_2O$) C, H, S.

Reactions of Sulfurane 18. (a) With *tert*-Butyl Hypochlorite. To a solution of **18** in $CDCl_3$, 1 drop of *tert*-butyl hypochlorite was added. After 30 min, persulfurane **27** was formed, as observed by the ^{1}H NMR.

(b) With MCPBA. To a solution of **18** in $CDCl_3$, excess MCPBA was added. After 5 days, the peaks for the two diastereotopic geminal methyl groups appeared at δ 1.78 and 1.58, and the *tert*-butyl groups at 1.41 in the ^{1}H NMR spectrum, similar to those of sulfurane oxide diacid **25**.

(c) With Diazomethane. To a suspension of **18** (50 mg, 0.1 mmol) in ether–CH_2Cl_2 was added a solution of CH_2N_2 in ether until no further N_2 evolved. Removal of solvent gave a solid, which was recrystallized from ether–pentane to give crystals of sulfurane diester **28**: 40 mg (0.076 mmol, 76%); mp 202–204 °C; ^{1}H NMR ($CDCl_3$) δ 7.48 (d, 2, Ar H), 7.11 (d, 2, Ar H), 3.92 (s, 6, OCH_3), 1.32 (s, 24, $OCCH_3$ and $C(CH_3)_3$), 1.07 (s, 6, $OCCH_3$). Anal. ($C_{30}H_{42}O_6S$) C, H.

(d) With *l*-(−)-α-Phenylethylamine. A solution of **18** (1.28 g, 2.56 mmol) and the optically active amine (0.31 g, 2.56 mmol) was boiled for 4 h. Removal of solvent gave a residue, which was crystallized from ethyl acetate and washed with ether to give crystals of the salt of **18**: 600 mg (0.966 mmol, 37.7%); mp 192–194 °C; ^{1}H NMR ($CDCl_3$) δ 8.1–7.0 (m, 9, Ar H), 6.1 (br, 4, NH_3 and OH), 4.0 (q, 1, CH_3CH), 1.85 (slightly br s, 6, $OCCH_3$), 1.73 (br s, 6, $OCCH_3$), 1.29 (br s, 21, $C(CH_3)_3$ and CH_3). Anal. ($C_{36}H_{47}NO_6S$) C, H, N, S.

7,7′-Dicarboxy-5,5′-bis(1,1-dimethylethyl)-3,3,3′,3′-tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxathiole] 1-Oxide (25). To a suspension of **18** (1.35 g, 2.7 mmol) in ether–THF was added powdered KH (ca. 0.63 g, 15.2 mmol, excess). After 14 h, the suspension was carefully decanted to leave most of the unreacted KH behind. The solvent was removed under vacuum to leave a solid, which was washed with pentane and dried under vacuum (100 °C) to give the crude dipotassium salt of **18** (**21**): 1.775 g (some KH might be trapped); IR (Nujol) 1567 (br, s, C=O) cm^{-1}; ^{1}H NMR (D_2O, H_2O at δ 4.61 as reference) δ 7.11 (br s, 2, Ar H), 6.87 (br s, 2, Ar H), 1.30 (s, 6, $OCCH_3$), 1.27 (s, 18, $C(CH_3)_3$, 1.14 (s, 6, $OCCH_3$); ^{13}C NMR (D_2O) 177 (C=O), 156, 151.8, 142.4, 135.2, 124.9, 119.0 (Ar C), 80.0 ($OC(CH_3)_2$), 34.9 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 30.3 ($OCCH_3$), 28.4 ($OCCH_3$).

Ozone was bubbled through a solution of sulfurane dipotassium salt **21** in water for 0.5 h at room temperature to give sulfurane oxide dipotassium salt **23**: ^{1}H NMR (D_2O) δ 7.35 (d, 2, Ar H), 7.30 (d, 2, Ar H), 1.71 (s, 6, $OCCH_3$), 1.50 (s, 6, $OCCH_3$), 1.32 (s, 18, $C(CH_3)_3$). The aqueous solution of **23** was acidified with dilute HCl and extracted with $CHCl_3$. The $CHCl_3$ solution was dried (Na_2SO_4), and the solvent was removed to give crude sulfurane oxide diacid **25**: 1.0 g (1.74 mmol, 64.3%); ^{1}H NMR ($CDCl_3$) δ 7.95 (d, 2, Ar H), 7.33 (d, 2, Ar H), 1.78 (s, 6, $OCCH_3$), 1.58 (s, 6, $OCCH_3$), 1.41 (s, 18, $C(CH_3)_3$). Attempts to purify the product by recrystallization, however, resulted in fragmentation of **25** to give isomeric sulfone diacid: ^{1}H NMR ($CDCl_3$) δ 7.38–7.36 (s and d, 3, Ar H), 7.2 (d, 1, Ar H), 6.83 (br, 3, OH), 4.95 (br s, 1, olefinic CH), 4.62 (br s, 1, olefinic CH), 1.85 (s, 3, CH_3C=C), 1.60 (s, 3, $OCCH_3$), 1.44 (s, 3, $OCCH_3$), 1.33 (s, 9, $C(CH_3)_3$), 1.30 (s, 9, $C(CH_3)_3$).

7-Carbethoxy-7′-(1-hydroxy-1-methylethyl)-5,5′-bis(1,1-dimethylethyl)-3,3-dimethyl-3′-oxo-1,1′-spirobi[3*H*-2,1-benzoxathiole] (19). A solution of MCPBA (1.53 g of 85% peracid, 7.55 mmol) in $CDCl_3$ was added in one portion to a solution of sulfide **11** (ca. 4 g, 7.55 mmol) in $CDCl_3$. After 1 h, the solution was extracted with aqueous $NaHCO_3$ and dried (Na_2SO_4). Removal of solvent gave a solid, which was recrystallized from ether–pentane to give crystals of sulfurane **19**: 3 g (5.66 mmol, 75%); mp 192.5–193.5 °C; IR ($CHCl_3$) 3365 (br, m), 1727 (s, C=O), 1642 (s, C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.16 (d, 1, Ar H), 7.53 (d, 1, Ar H), 7.33 (d, 1, Ar H), 7.03 (d, 1, Ar H), 3.08–3.0 (m, 3, OCH_2CH_3), 1.95 (s, 3, $OCCH_3$), 1.89 (s, 6, $OCCH_3$), 1.58 (s, 3, $OCCH_3$), 1.45 (s, 9, $C(CH_3)_3$), 1.31 (s, 9, $C(CH_3)_3$), 1.14 (t, 3, OCH_2CH_3); mass spectrum (3.5 eV), *m/e* (relative intensity) 528 (M^+, not observed), 513 (15.2, $M^+ - CH_3$), 469 ($M^+ - (CH_3)_2OH$), 446 (100).

Sulfide **11** was probably obtained from hydrolysis of sulfide diester diol **2** during its crystallization from ethanol–water, but was not purified and fully characterized. ^{1}H NMR ($CDCl_3$) of **11**: δ 7.6 (d, 1, Ar H), 7.52 (d, 1, Ar H), 7.42 (d, 1, Ar H), 7.28 (d, 1, Ar H), 4.95 (br, 2, OH), 3.95–3.15 (m, 3, OCH_2CH_3), 1.84 (s, 6, $OCCH_3$), 1.74 (s, 6, $OCCH_3$), 1.34 (s, 9, $C(CH_3)_3$), 1.24 (s, 9, $C(CH_3)_3$), 1.05 (t, 3, OCH_2CH_3).

Potassium Salt of Sulfurane 19 (22). Powdered KH (ca. 70 mg, 1.74 mmol) was added to a stirred solution of sulfurane **19** (550 mg, 1.04 mmol) in THF. After 6 h, the solution was filtered and removal of solvent gave a brown solid: 540 mg (95.3 mmol, 92%); IR (Nujol) 1730 (s, C=O), 1597 (s, C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.4 (d, 2, Ar H), 7.0 (d, 1, Ar H), 6.84 (d, 1, Ar H), 4.25 (q, 2, OCH_2CH_3), 2–0.6 (br m, 33, all CH_3).

Reaction of 19 with Iodomethane. Iodomethane (0.2 mL, 3 mmol) was added to a solution of potassium salt **15** (120 mg, 0.21 mmol) in 10 mL of THF. After 10 h, the solution was filtered, and the solvent was removed to leave a solid, which was recrystallized from ether–pentane by slow evaporation to give crystals of sulfurane diester **29**: 98 mg (0.18 mmol, 85.8%); mp 187–188 °C; IR ($CHCl_3$) 1724 (s, C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.48 (d, 2, Ar H), 7.1 (d, 2, Ar H), 4.37 (q, 2, J = 7.1 Hz, OCH_2CH_3), 3.95 (s, 3, OCH_3), 1.44 (t, 3, J = 7.1 Hz, OCH_2CH_3), 1.31 (s, 24, $C(CH_3)_3$) and $OCCH_3$), 1.07 (s, 6, $OCCH_3$).

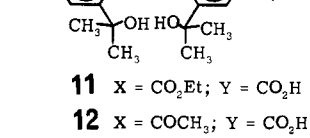
Reaction of Sulfurane Diester 29 with Methyllithium. A solution of CH_3Li–LiBr in ether (0.56 mL of a 2 M solution, 1.12 mmol) was added to a solution of **29** (74.6 mg, 0.137 mmol) in ether. After 24 h, the solution was quenched with water, the ether layer was separated and dried (Na_2SO_4), and the solvent was removed to give a solid, which was a mixture of benzenediol **32** and dioxosulfurane **31** (by NMR). Recrystallization from ether–pentane afforded crystals of **31**: 32 mg (0.064 mmol, 47%); mp 176–180 °C dec; IR ($CHCl_3$) 1689 (s, C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.32 (d, 2, Ar H), 7.14 (d, 2, Ar H), 2.66 (s, 6, $COCH_3$), 1.40 (s, 6, $OCCH_3$), 1.34 (s, 18, $C(CH_3)_3$), 1.17 (s, 6, $OCCH_3$). Anal. ($C_{30}H_{40}O_4S$) C, H.

Reaction of Potassium Salt with Ozone. Ozone was bubbled into a solution of **22** (250 mg, 0.44 mmol) in CH_2Cl_2 at −78 °C until the solution turned blue. After the mixture warmed to room temperature, the solvent was removed to give a yellow residue, crude sulfurane oxide potassium salt **24**: 257 mg (0.44 mmol, 100%); IR (Nujol) 1726 (s, C=O), 1597 (s, C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.61 (d, 1, Ar H), 7.52 (d, 1, Ar H), 7.2 (d, 1, Ar H), 7.04 (d, 1, Ar H), 4.37 (q, 2, OCH_2CH_3), 1.58 (s, 6, $OCCH_3$), 1.51 (s, 6, $OCCH_3$), 1.37 (t, 3, OCH_2CH_3), 1.33 (s, 9, $C(CH_3)_3$), 1.28 (s, 9, $C(CH_3)_3$).

A solution of **24** (200 mg, 0.34 mmol) in CH_2Cl_2 was extracted with saturated NH_4Cl and with dilute HCl and dried (Na_2SO_4). The solvent was removed, and the resulting solid was washed with pentane to give sulfurane oxide acid **26**: 111 mg (0.2 mmol, 60%); mp 115–123 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.94 (d, 1, Ar H), 7.69 (d, 1, Ar H), 7.27 (d, 1, Ar H), 7.23 (d, 1, Ar H), 4.38 (q, 2, OCH_2CH_3), 1.76 (s, 3, $OCCH_3$), 1.69 (s, 3, $OCCH_3$), 1.53 (s, 3, $OCCH_3$), 1.51 (s, 3, $OCCH_3$), 1.37 (s, 18, $C(CH_3)_3$). Anal. ($C_{30}H_{36}O_7S$) C, H, S.

Results

Synthesis. The syntheses of sulfides **1**, **2**, and **4** have been reported earlier.[1] From the preparation of sulfide diester **2** and its subsequent hydrolysis to give sulfide diacid **4**, minor products such as sulfides **11** and **12** were

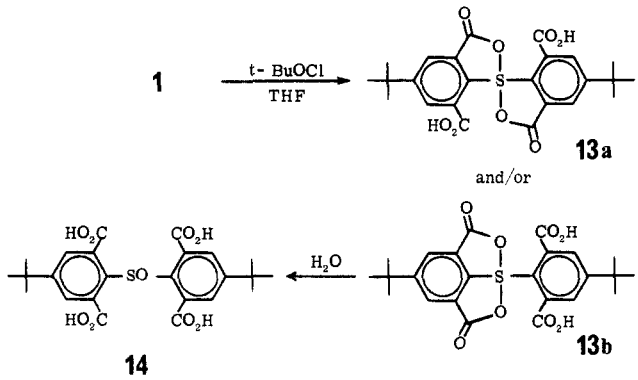


11 X = CO_2Et; Y = CO_2H

12 X = $COCH_3$; Y = CO_2H

obtained in small quantities. Treatment of **1** with *tert*-butyl hypochlorite gave bis(acyloxy)sulfurane **13**. An analogue of **13a**, without the *o*-carboxy and *tert*-butyl substituents, has been reported.[4] The ^{1}H NMR spectrum

(4) Kapovits, I.; Kálmán, A. *Chem. Commun.* **1971**, 649.

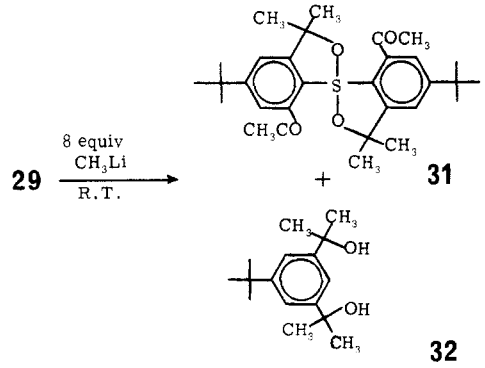


of **13** at room temperature shows a singlet at δ 8.1 corresponding to the aromatic protons, instead of the AB pattern expected for structure **13a** or **13b**. Sulfurane **13** is easily hydrolyzed to give sulfoxide tetraacid **14**.

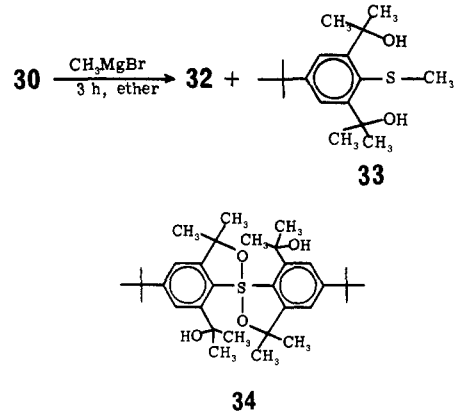
Unsymmetrical sulfuranes **18–20** were synthesized by reactions of sulfides **4**, **11**, and **12**, respectively, with *m*-chloroperbenzoic acid (MCPBA; see Scheme I).

Sulfoxide diols **15–17**, the expected products of these peracid oxidations, if they are indeed formed, undergo cyclodehydration to give sulfuranes **18–20**, respectively, too rapidly to permit isolation. It is, of course, possible to envision mechanisms for the oxidations which bypass the sulfoxides. Treatment of sulfuranes **18** and **19** with KH give the corresponding potassium salts **21** and **22**, respectively, as evidenced by ^1H and ^{13}C NMR and by reactions of **21** and **22** with ozone to give sulfurane oxides **23** and **24**. These, upon acidification, give sulfurane oxides **25** and **26**, respectively (Scheme II). Sulfurane oxides **25** and **26**, like analogous reported dialkoxysulfurane oxides,[3,5] slowly undergo fragmentation to form isomeric sulfonyl hydroxyolefins.

Reactions. Hydroxy acid sulfurane **18** reacts with *tert*-butyl hypochlorite, with diazomethane, and with MCPBA to form persulfurane **27**, sulfurane diester **28**, and sulfurane oxide **25**, respectively (Scheme III). It also forms a crystalline salt with optically active *L*-(−)-1-phenylethylamine. Attempts to separate the diastereotopic salts by fractional recrystallization have not been successful. Sulfurane **18** failed to form a crystalline salt with strychnine or brucine. Monopotassium salt **22** reacts with CH_3I to give sulfurane diester **29**, whereas sulfurane keto alcohol **20** reacts with CH_2N_2 to give **30**. Treatment of **29** with 8 equiv of CH_3Li gave dioxosulfurane **31** and benzenediol **32**, whereas treatment of **30** with excess CH_3MgBr afforded



32 and methyl sulfide **33**. In neither reaction was sulfurane diol **34** observed. The observed products such as **32**



and **33** can be explained by postulating attack of the organometallic reagent at the sulfur atom.

All sulfuranes having two identical apical alkoxy ligands such as **28–31** have proved to be readily oxidized with MCPBA to give the corresponding sulfurane oxides, as observed as NMR. Unsymmetrically substituted sulfurane oxides with different apical ligands have not been prepared.[1b,5]

^1H NMR Observations on 18. The ^1H NMR spectrum of hydroxy acid sulfurane **18** at room temperature in $CDCl_3$ or Me_2SO-d_6 solvent showed two broad methyl singlets and a broad *tert*-butyl singlet. At higher temperature, these broad peaks were narrowed into sharp singlets. Meanwhile, the broad aromatic peaks were transferred into well-defined AB doublets. Studies at higher temperature were prevented by the fact that rather rapid decomposition of **18** was observed at temperatures above 140 °C. When the sample was cooled stepwise, the two broad methyl singlets and the broad *tert*-butyl peak were further broadened and then resolved into several sharp singlets. At −18 °C, the two broad methyl peaks were resolved into three singlets corresponding to the four nonequivalent methyl groups, with two of them accidentally having the same chemical shift, whereas the *tert*-butyl peak was resolved into two sharp singlets. Meanwhile, the aromatic signals became four doublets. From the coalescence temperature (12 °C) and the chemical shift separation of the two *tert*-butyl singlets (13.8 Hz), a $\Delta G^{\ddagger}$ of ca. 14.7 kcal mol^{-1} at 12 °C was calculated.[6]

The room-temperature ^1H NMR spectrum of **18**, in Me_2SO-d_6 containing 1 drop of concentrated aqueous HCl or in $CDCl_3$ containing 1 drop of trifluoroacetic acid, was very similar to that of **18** in $CDCl_3$ at −18 °C. Coalescence of the two *tert*-butyl singlets occurred at ca. 65 °C, a temperature much higher than the coalescence temperature of the two *tert*-butyl singlets in nonacidic media.

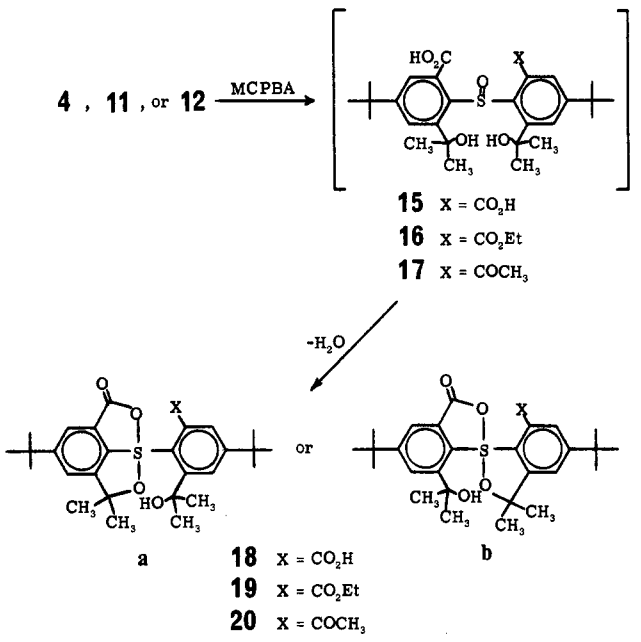
Addition of about 20% (v/v) of optically active 2,2,2-trifluoro-1-phenylethanol[7] to a $CDCl_3$ solution of **18** (−30 °C) resulted in the resolution of each of the two *tert*-butyl singlets seen in the 220-MHz ^1H NMR spectrum of a sample in achiral medium (1.26 and 1.41 ppm) into two peaks of equal area separated by about 0.02 ppm. This clearly demonstrates the chirality of the conformers of **18** frozen out at −30 °C.

Discussion

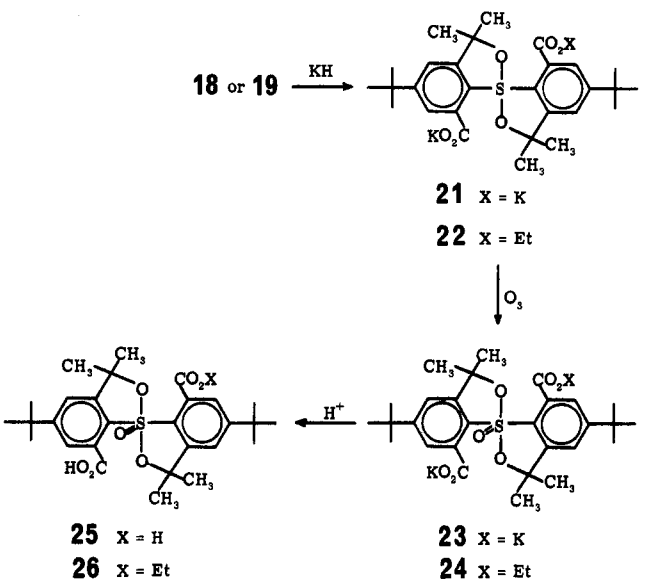
Apical Ligand Preference. The structures of sulfuranes **18–20** having unsymmetrically substituted apical positions were established by infrared and ^1H and ^{13}C NMR spectroscopy.

(5) (a) Adzima, L. J.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 1657. (b) Lau, P. H. W.; Martin, J. C. *Ibid.* **1977**, *99*, 5490.
(6) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.
(7) (a) Pirkle, W. H.; Muntz, R. L.; Paul, I. C. *J. Am. Chem. Soc.* **1971**, *93*, 2817. (b) Pirkle, W. H.; Sikkenga, D. L. *J. Org. Chem.* **1975**, *40*, 3430.

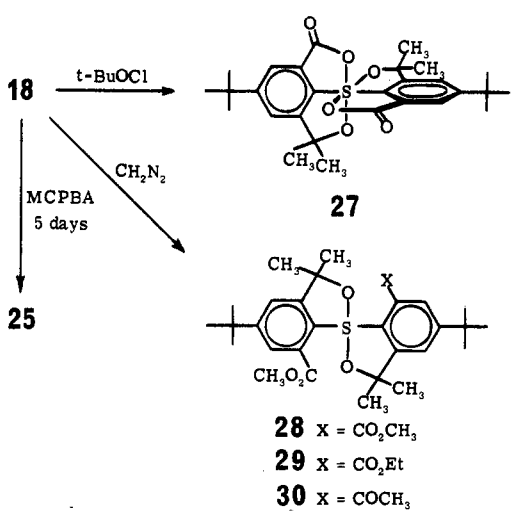
Scheme I



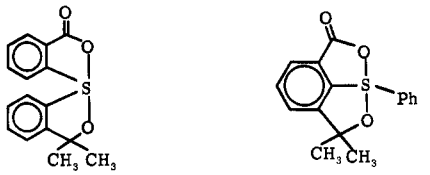
Scheme II



Scheme III



The three-center four-electron hypervalent bonds in sulfuranes are very polarizable.[8] The polarization in such species bearing two different apical ligands is reflected in the carbonyl stretching frequencies of apical acyloxy ligands[8] or the chemical shifts of the quaternary carbons in apical tertiary alkoxy ligands.[9] For **19** and **20**, two carbonyl stretching frequencies were seen for each compound, with one of them at the low frequency expected[8] for the absorption of the acyloxy ligand (1642 and 1637 cm^{-1}, respectively). A broad carbonyl absorption, centered at 1615 cm^{-1}, was observed for **18**. These absorptions are very close to those of other similarly unsymmetrical sulfuranes such as **35** (1647 cm^{-1}) and **36**[1b] (1639 cm^{-1}). In these species,

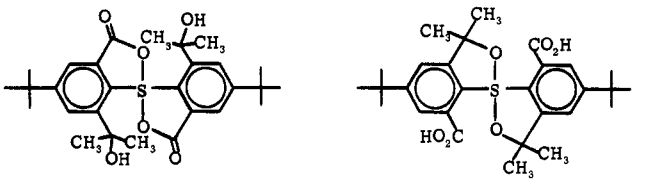


35 **36**

the acyloxy ligand is effectively more electronegative than the alkoxy ligand. Electron density is expected[8] to be removed from the alkoxy ligand toward the acyloxy ligand, resulting in a greater resemblance to a carboxylate anion in its carbonyl stretching frequency than is found when the alkoxy ligand is replaced by a more electronegative group.

The quaternary carbons of the apical alkoxy ligands in sulfuranes **18–20** showed ^{13}C chemical shifts of 97.3 (at −40 °C), 93.2, and 94.4 ppm, respectively, very close to those in **35** (92.0 ppm) and **36** (95.6 ppm).[9] All are further downfield than in analogous free alcohols such as **2**, **3**, or **4** (around 75 ppm). This is consistent with the fact that sulfuranes **18–20** have unsymmetrically substituted apical ligands. Whether these sulfuranes are in the bicyclic form (**a**) or the spiro form (**b**), however, cannot be determined since the IR and NMR spectral evidence is consistent with either structure.

Structures **18c** and **18d** are the other two possible permutational isomers of **18**. That these are not favored at equilibrium is evidenced by IR and NMR spectroscopy. One would have expected[8] the symmetrical diacyloxysulfurane isomer **18c** to have a carbonyl absorption at



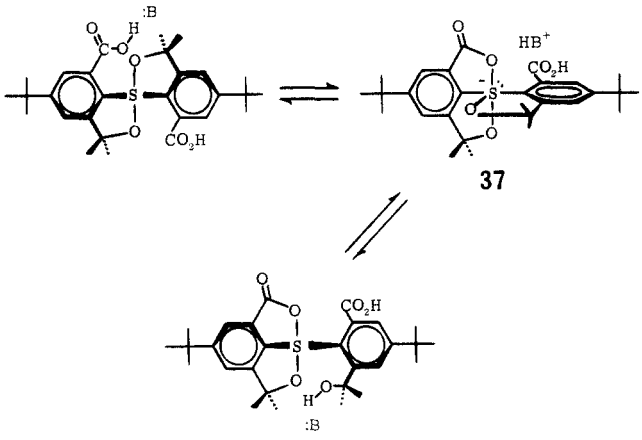
18c **18d**

about 1724 cm^{-1} (vs. 1615 cm^{-1} observed). The quaternary carbon of the apical alkoxy ligands in isomer **18d** would be expected[9] to be about 80 ppm (vs. 97.3 ppm observed).

One factor which might be expected to be important in determining the order of relative stabilities of **18a** or **18b**, **18c**, and **18d** is the effective electronegativities of apical ligands (acyloxy > alkoxy). It has long been known[10] that trigonal-bipyramidal species are more stable when the apical positions are occupied by more electronegative ligands. This factor alone would predict an order of stabilities of **18c** > **18(a** or **b)** > **18d**. On the other hand, the hy-

(8) Livant, P.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 5761.
(9) Lam, W. Y.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 1927.
(10) Musher, J. I. in *Adv. Chem. Ser.* **1972**, *No. 110*, 42.
(11) (a) Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 1535. (b) Sabacky, M. J.; Johnson, S. M.; Martin, J. C.; Paul, I. C. *Ibid.* **1969**, *91*, 7542.

Scheme IV



pervalent bond of the symmetrical **18c** is much less polarized than that of **18a** or **18b**.[8] The acyloxy ligands bear much less negative charge in **18c** than in **18a** or **18b**, a factor which would tend to make **18a** or **18b** more stable than the average of **18c** or **18d**. Indeed, this factor provides the simplest explanation for the apparent greater stability of **18a** or **18b**. Thus the lack of a highly polarized hypervalent bond in **18c** may be an energetically unfavorable structural feature.

The fact that potassium salts of sulfuranes **18** and **19** (**21** and **22**, respectively) have the symmetrically substituted dialkoxy sulfurane structures as the ground-state conformation is not surprising. The initial alkoxide products of reactions of **18** and **19** with KH undergo associative displacements of the carboxylate groups at sulfur to give isomeric structures **21** and **22**. Structure **21** and **22** are favored because full negative charges are placed on the more electronegative carboxylate groups. Upon acidification of potassium salts **21** and **22** the original isomers **18** and **19**, respectively, are recovered. This clearly demonstrates that the unsymmetrically substituted sulfuranes **18** and **19** are indeed the preferred ground-state isomers.

Intramolecular Ligand Exchange and Fluxional Behavior. An associative mechanism such as that shown in Scheme IV is postulated to be responsible for the rapid intramolecular ligand exchanges in sulfurane **18**, as observed by NMR. The transfer of a proton to a base is accompanied by nucleophilic attack on sulfur by the carboxy group to form an intermediate or transition state, **37**, which may lose one of the three oxygen ligands to give a new isomer of **18**. Evidence for this associative mechanism for exchange lies in the observation that the rapid permutational isomerization observed for **18** by ^{1}H NMR is markedly slowed by the introduction of acid into the medium.

The low-temperature NMR spectrum of **18** shows three methyl singlets corresponding to the four nonequivalent methyl groups (two of them accidentally having the same chemical shift) and two *tert*-butyl singlets for the *tert*-butyl groups of structure **18** [this is consistent with either the bicyclic (**a**) or the spiro structure (**b**) for **18**]. The postulated rapid interconversion processes at higher temperatures which produce coalescence of the three methyl singlets into two singlets and of the two *tert*-butyl singlets into one singlet, are shown in Figure 1, reactions presumed to occur by a mechanism similar to that of Scheme IV. The interconversions are of permutational isomers A and B and isomers C and D, involving only rotations about one C–S bond with the small barrier resulting primarily from interactions between an ortho substituent of the mobile ring with C_1 or the aromatic ring in the fused-ring system.

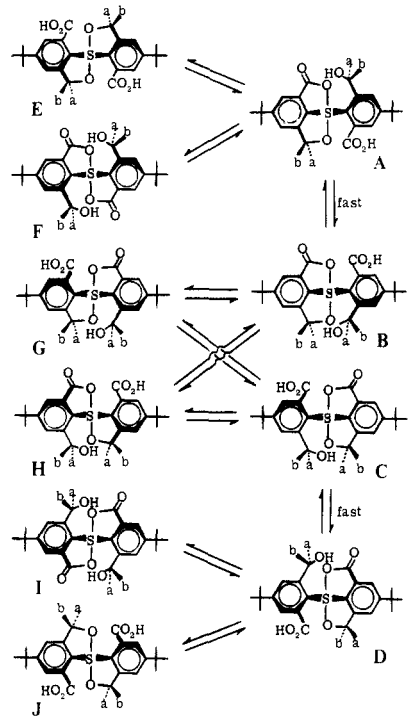


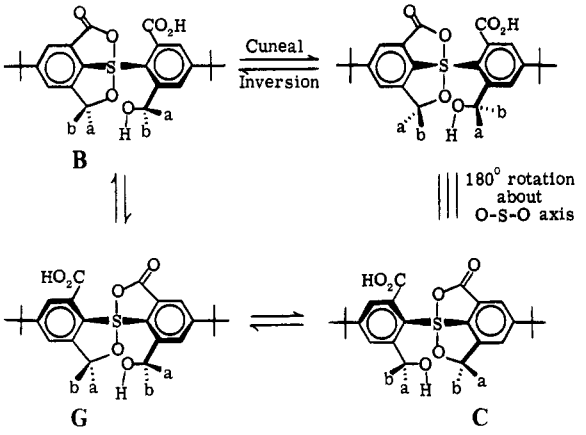
Figure 1. Proposed mechanism for the process in which the three methyl singlets and the two *tert*-butyl singlets coalesce into two methyl singlets and a *tert*-butyl singlet, respectively, as observed in high-temperature NMR. Note that the pictured process preserves the identities of methyl groups a and b.

These are fast processes even at low temperature. Each of these bicyclic isomers (A–D) can undergo rapid interconversions with two spiro isomers (E–J, Figure 1). In the case of B and C, both interconvert with the same two spiro isomers (G and H). In these processes, the alcohol oxygen or the carboxyl oxygen displaces an apical ligand by a nucleophilic attack on sulfur. Meanwhile the aryl rings undergo a "gear-meshing" or conrotatory mode of synchronous internal rotation.[11] This avoids the large repulsive interaction which would result from the close approach of an ortho substituent to an apical substituent in a conrotatory mode of synchronous ring rotation. In these rapid, low-barrier processes ($\Delta G^{\ddagger}_{12°C}$ = 14.7 kcal mol^{-1}) of equilibration of isomers via pathways shown in Figure 1, one set of geminal methyl groups in the alkoxy substituent becomes magnetically equivalent to the other, but methyl groups a and b do not interconvert. The slower equilibration of the isomers of **18** in acidic medium is consistent with this proposed associative mechanism since the alcohol and carboxyl groups would be less nucleophilic in acidic medium.

We have simplified the scheme of Figure 1 by omitting those isomers of the spiro compounds which have one of the unattached ortho substituents endo and the other exo. An examination of molecular models suggest that these isomers would be higher in energy than the pictured exo–exo and endo–endo isomers.

Sulfurane **18** might also be imagined to follow a possible pathway for isomerization involving cuneal inversion[3] at sulfur at higher temperature (Scheme V). It is interesting to note (Scheme V) that this process, whose transition state would have the four bonds to sulfur coplanar, also fails to interconvert the two diastereotopic methyl groups a and b, as long as the process does not involve "gear-clashing" conrotatory synchronous ring rotations at the same time as the cuneal inversion. Isomer B, for example, undergoes a cuneal inversion only to become isomer C, which then

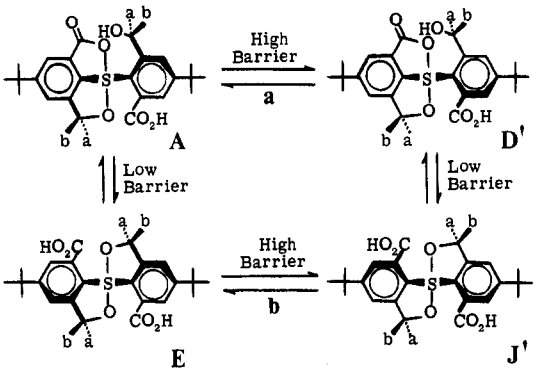
Scheme V



rapidly equilibrates with other isomers by processes represented in Figure 1. The earlier discussions[3] of cuneal inversions envisioned a transition state with square-planar tetracoordinate sulfur. Such a process could, like the rotation of Scheme IV, show base catalysis if it could proceed by way of a transition state such as **37**. The intramolecular association of a nucleophile with the sulfur could, as in **37**, result in the four bonds of the sulfuranyl sulfur becoming essentially coplanar. The microscopic reverse of this process would, of course, regenerate starting material, but it is possible that a competing mode of reaction of **37** would result in inversion at sulfur. Such a process of neighboring nucleophile-assisted cuneal inversion could occur, but as is shown in Scheme V it could not explain the observed results because it does not result in the interconversion of methyl groups. It would do so only if it were accompanied by a "gear-clashing" mode of internal rotation of the two aryl rings through a transition state with a large degree of steric interference between the ortho substituents of the free aryl ring with the apical substituents at sulfur. Another high-barrier process via a pathway such as b (E $\rightleftharpoons$ J′ process, Scheme VI) which would interchange the two nonequivalent methyl peaks also requires a "gear-clashing" mode of concerted internal rotation of the two aryl rings. It can be seen from Figure 1 that structures D′ and J′, which are enantiomeric to D and J, respectively, are members of a set of rapidly equilibrating isomers which are enantiomeric to the set pictured in Figure 1. It can also be seen that the identities of the diastereotopic methyl groups have been interchanged in this set of isomers. At temperatures high enough to make these processes rapid, the two methyl singlets would coalesce.

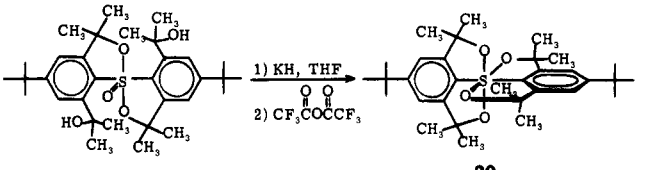
Attempts to Resolve Sulfurane 18. The enantiomers in racemic sulfurane **18** are separately observed by NMR in chiral medium at room temperature. Since they form salts with amines, we tried to resolve sulfurane **18** via diastereotopic salts of enantiomerically pure amines.

Scheme VI



Several attempts to resolve the mixtures of such salts formed with *l*-(−)-α-phenylethylamine failed. Further work will be directed to a solution of this problem. It is expected that optically active **18** might serve as a precursor to optically active persulfurane **27**. The rather large barrier (>21.3 kcal mol^{-1}) observed for interconversion of the geminal methyl groups in the NMR of **18** suggests that the racemization of optically active **18**, the same process which interconverts the methyl groups, should be slow enough to allow chemical resolution of enantiomeric families of rapidly interconverting isomers. Each of these resolved families of isomers would be expected to react with *tert*-butyl hypochlorite at low temperature in the same manner as sulfide **4**, to give optically active persulfurane **27**.

Another unsuccessful approach to optically active persulfurane **27** was from sulfurane oxide diacid **25**, which one might expect to undergo cyclodehydration to give **27** under appropriate conditions.[1b] The cyclodehydration of sulfurane oxide diol **38** to form persulfurane **39** has been re-



ported.[1b] However, **25** was found to undergo fragmentation in solution sufficiently rapid to make it impractical to use this route for the resolution of **25**.

Acknowledgment. This research is supported in part by a grant from the National Science Foundation (CHE-790592).

Registry No. **2**, 62558-12-7; **4**, 62558-13-8; **11**, 78514-65-5; **12**, 78514-66-6; **18a**, 78514-67-7; **18b**, 78514-68-8; **19a**, 78514-69-9; **19b**, 78514-70-2; **20c**, 78514-71-3; **20b**, 78529-82-5; **21**, 78514-72-4; **22**, 78514-73-5; **23**, 78514-74-6; **24**, 78514-75-7; **25**, 78514-76-8; **26**, 78514-77-9; **27**, 62572-48-9; **28**, 78514-78-0; **29**, 78514-79-1; **31**, 78514-80-4.