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Sulfuranes Lacking Benzoannelation. Sulfuranes and Other Hypervalent Molecules Studied by ^{17}O-NMR

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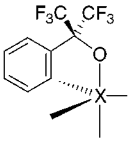
The rates of hydrolysis of benzoannelated vs nonbenzoannelated sulfuranes, viz. **5** vs **3** or **5** vs **4**, were compared. Benzoannelation was found to provide very modest kinetic stabilization. Crystal structures of sulfuranes **3** and **4** were obtained and compared with each other, with a dibenzoannelated sulfurane, **17**, and with a non-sulfurane analogue of **4**. Bond length variations could be understood in the context of simple resonance arguments. ^{17}O NMR studies of **3**−**5** showed that this technique was indeed sensitive to sulfurane structure. For example, the chemical shifts of the two carbonyl oxygens of **4** differed by over 20 ppm. Other hypervalent systems, mainly iodinanes, were studied by ^{17}O NMR. A variety of theoretical methods were surveyed to test how well they could reproduce the geometry of **3**. Density functional theory calculation outperformed ab initio geometry optimization at the MP2/3-21G(*) level. Finally, a cis−trans isomerization of the double bond of **11** and one of the two double bonds of **10** was studied.

Introduction

Because of all the seminal work in sulfurane chemistry by J. C. Martin and co-workers, the vast majority of known sulfuranes embody principles of design which he enunciated.[2] These include the presence of a five-membered ring spanning equatorial and apical positions of the trigonal bipyramid, apical groups of high electronegativity, *gem*-dialkyl groups on the five-membered ring, and benzoannelation of the five-membered ring. This recipe implies generic structures **1** and **2**, which have been used with great success by Martin and his group in numerous instances. Indeed, recent workers refer to **2** as simply "the Martin ligand."[3]



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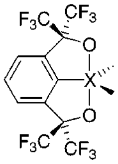

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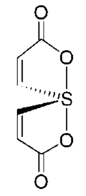
The necessity of benzoannelation came into question in our laboratories as an outgrowth of our interest in ^{17}O NMR studies of sulfuranes. Our early attempts to obtain ^{17}O NMR spectra of sulfuranes were unsuccessful. This failure, we reasoned, may have been due to the sheer bulk, and consequently the longer rotational correlation times, of the sulfuranes under study, all of which contained phenyl rings. Therefore, we considered simply leaving off the phenyl ring(s) to allow the molecule to tumble faster. Target sulfuranes **3** and **4** were devised to help solve our ^{17}O NMR problem. It then followed naturally that the question of the necessity of benzoannelation in sulfurane design could be addressed by measuring the relative kinetic stabilities of the sulfuranes in the series **3**−**5**.



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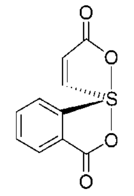

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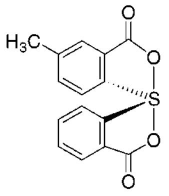

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Experimental Section

(*Z,Z*)-3,3′-Thiodi(propenoic acid), 6. To a cooled (0 °C) solution of 98% *meso*-dibromosuccinic acid (49.9 g, 177 mmol) in 114 mL of absolute ethanol was added a solution of 55.00 g (835 mmol) of 85% KOH pellets in 150 mL of ethanol. The resulting mixture was refluxed 2 h. The mixture was filtered while hot and washed twice with boiling ethanol. The filter cake was dissolved in 120 mL water and acidified at 0 °C by slow addition of 25% (v/v) aq H_2SO_4 to pH < 2. The precipitate was vacuum filtered, suspended in 150 mL of water, and heated to reflux for 3 h. A small amount of solid remaining in the reaction mixture was removed by filtration at room temperature, and the filtrate was cooled to 10 °C. This was treated with a solution of 10.0 g (152 mmol) of 85% KOH pellets in 70 mL of water until pH > 10, followed by gradual addition of 22.3 g (92.9 mmol) $Na_2S{\cdot}9H_2O$. This mixture was stirred under N_2 1 h at 10 °C and then 12 h at room temperature. The solution was acidified at 0 °C by addition of ice-cold 10% (v/v) aq H_2SO_4 to pH < 2. The resulting precipitate was collected by vacuum filtration, washed twice with water, and dried on the vacuum line, to give 7.94 g **6**, 51.5% yield. mp 233.5−235 °C. (lit.[4] 245−247 °C (dec), 244−245 °C) IR (KBr): 1673, 1592, 1561, 897, 810 cm^{-1}. ^{1}H NMR (acetone-d_6): 7.591 (d, $J = 10.3$ Hz, 1H), 6.041 (d, $J = 10.3$ Hz, 1H) ^{13}C NMR (acetone-d_6): 167.10 (quat), 150.06 (CH), 116.09 (CH).

1,1′-Spirobi(2,1-oxathiol-3-one), 3. All manipulations were performed in a N_2-filled glovebox. To a stirred solution of 1.00

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g (5.75 mmol) of **6**, 6.10 g (77.2 mmol) of dried pyridine, and 29.0 g of dried chloroform was added dropwise 680 mg (6.30 mmol) *tert*-butyl hypochlorite (prepared by the method of Walling and Mintz[5]). After stirring for 3 min, the mixture was vacuum filtered. The collected solid was washed twice with dry pentane and dried on the vacuum line, to give 654 mg of **3**, 66% yield. mp 160.5−161 °C. IR (KBr): 3108, 3067, 1707, 1188, 1080 $\mathrm{cm^{-1}}$. ^{1}H NMR (acetone-d_6): 7.778 (d, $J = 5.2$ Hz, 1H), 7.194 (d, $J = 5.2$ Hz, 1H) ^{13}C NMR (acetone-d_6): 167.17 (quat), 146.79 (CH), 134.77 (CH). ^{17}O NMR (59.4 MHz, $\mathrm{CH_2Cl_2}$): 344 (C═O), 273 (−O−).

X-ray Structure of 3. Sulfurane **3** was recrystallized from an acetone−$\mathrm{CCl_4}$ mixture at low temperature under strictly anhydrous conditions. A rhomboidal plate of approximate dimensions 0.50 × 0.22 × 0.10 mm was selected; monoclinic, $a = 10.839(5)$ Å, $b = 4.337(2)$ Å, $c = 14.605(7)$ Å, $\beta = 105.41(3)°$, $V = 662.0(5)$ Å^3, $Z = 4$. Space group $C2/c$. 698 reflections (581 independent, $R_{\mathrm{int}} = 2.47\%$) were collected, of which 499 were considered observed, $F > 4.0\sigma(F)$. The structure was solved by direct methods and refined by full-matrix least squares (on F), giving $R = 0.0416$ and $wR = 0.0526$. An isotropic riding model was employed for hydrogens.

(*Z*,*Z*)-3,3′-Sulfinyldi(propenoic acid), 10. An acetone solution of sulfurane **3** was stirred for 1 d in a vessel open to the air. Removal of solvent and drying on the vacuum line afforded a quantitative yield of sulfoxide diacid **10**, mp 132.5−133 °C. IR (KBr): 1732, 1684 $\mathrm{cm^{-1}}$. ^{1}H NMR (acetone-d_6): 7.056 (d, $J = 10.4$ Hz, 1H), 6.500 (d, $J = 10.4$ Hz, 1H) ^{13}C NMR (acetone-d_6): 165.20 (quat), 150.76 (CH), 128.12 (CH).

Potassium 2-Mercaptobenzoate. To a solution of 30.0 g (191 mmol) of 98% 2-mercaptobenzoic acid in 90 mL of ethanol at 0 °C was gradually added 12.0 g (182 mmol) of 85% KOH pellets. After 30 min stirring at 0 °C, the precipitate was filtered and dried in vacuo. This material was used directly in the preparation of **7**.

(*Z*)-3-(2-Carboxyphenylthio)-2-propenoic Acid, 7. A solution of 10.0 g (35.5 mmol) of 98% meso-2,3-dibromosuccinic acid in 20 mL of absolute ethanol was cooled to 0 °C and treated gradually with a solution of 10.0 g (152 mmol) of 85% KOH pellets in 30 mL of ethanol. The mixture was refluxed 1 h and hot-filtered, washing the filter cake twice with boiling ethanol. The filter cake was dissolved in 26 mL of water, cooled to 0 °C, and treated slowly with ice-cold 25% (v/v) aq $\mathrm{H_2SO_4}$ until the pH was less than 2. The resulting precipitate was vacuum-filtered, suspended in 28 mL water, and refluxed 3 h. After cooling to 10 °C, it was treated with 4.37 g (22.8 mmol) of potassium 2-mercaptobenzoate and stirred 1 h while cold and then overnight at room temperature. It was filtered, and the filtrate, cooled to 0 °C, was acidified with ice-cold 10% (v/v) aq $\mathrm{H_2SO_4}$ to pH < 2. The precipitate which formed was suction-filtered, washed with water, and dried on the vacuum line, affording 3.55 g (44.6% yield) of diacid **7**, mp 184−186 °C. IR (KBr): 1680, 1593, 1582, 1565 $\mathrm{cm^{-1}}$. ^{1}H NMR (acetone-d_6): 7.943 (dd, $J = 7.8$, 1.5 Hz, 1H), 7.69−7.61 (m, 2H), 7.543 (d, $J = 10.2$ Hz, 1H), 7.453 (dt, $J = 7.4$, 1.4 Hz, 1H), 6.042 (d, $J = 10.2$ Hz, 1H) ^{13}C NMR (acetone-d_6): 167.61 (quat), 167.16 (quat), 149.65 (CH), 139.34 (quat), 133.33 (CH), 133.00 (quat), 132.12 (CH), 131.29 (CH), 128.08 (CH), 115.21 (CH).

X-ray Structure of 7. Crystals were obtained by slow evaporation of a methanol solution of **7**, and a diamond-shaped crystal of approximate dimensions 0.20 × 0.22 × 0.22 mm was chosen; monoclinic, $a = 5.273(2)$ Å, $b = 13.846(5)$ Å, $c = 13.532(4)$ Å, $\beta = 97.53(3)°$, $V = 979.5(6)$ Å^3, $Z = 4$. Space group $P2_1/n$. A total of 1530 reflections (1292 independent, $R_{\mathrm{int}} = 9.54\%$) were collected, of which 1291 were taken to be observed ($F > 6.0\sigma(F)$). Solution and refinement were carried out as for **3**, giving R and wR of 0.0537 and 0.0623 respectively

2,1-Benzoxathiol-3-one-1-spiro-1′-(2′,1′-oxathiol-3′-one), 4. All manipulations were performed in a $\mathrm{N_2}$-filled glovebox. A solution of 1.00 g (4.46 mmol) of **7** and 360 mg (4.56 mmol) of dry pyridine in 45 mL of dry chloroform was stirred and treated gradually with a solution of 542 mg (5.00 mmol) of *tert*-butyl hypochlorite in 10 mL of dry chloroform. The resulting precipitate was vacuum filtered, washed sequentially with dry pentane and dry chloroform, and dried on the vacuum line. A 69.1% yield (684 mg) of **4** was obtained, mp 185.5−186.5 °C. IR (KBr): 1715 $\mathrm{cm^{-1}}$. ^{1}H NMR (acetone-d_6): 8.122 (d, $J = 7.2$ Hz, 1H), 8.022−7.946 (m, 3H), 7.981 (d, $J = 5.3$ Hz, 1H), 7.149 (d, $J = 5.3$ Hz, 1H) ^{13}C NMR (acetone-d_6): 167.43, 150.57, 140.54, 136.49, 134.95, 133.38, 132.19, 129.06, 128.88 ^{17}O NMR (59.4 MHz, $\mathrm{CH_2Cl_2}$): 343 (C═O), 320 (C═O), 278 (−O−), 266 (−O−).

X-ray Structure of 4. Sulfurane 4 was recrystallized from an acetone−$\mathrm{CCl_4}$ mixture at low temperature under strictly anhydrous conditions. A crystal of approximate dimensions 0.10 × 0.15 × 0.20 mm was selected; monoclinic, $a = 5.585(4)$ Å, $b = 17.216(7)$ Å, $c = 9.378(7)$ Å, $\beta = 91.16(6)°$, $V = 901.5(10)$ Å^3, $Z = 4$. Space group $P2_1/c$. 1373 reflections (1173 independent, $R_{\mathrm{int}} = 27.81\%$) were collected, of which 990 were considered observed, $F > 4.0\sigma(F)$. Solution and refinement were carried out as in the case of **3**, giving $R = 0.0734$ and $wR = 0.1076$.

(*Z*)-3-(2-Carboxyphenylsulfinyl)-2-propenoic Acid, 11. Sulfurane **4** was hydrolyzed by stirring an acetone solution of it for 2 d in a vessel open to the air. Removal of solvent and drying on the vacuum line afforded a quantitative yield of sulfoxide diacid **11**, mp 161−162 °C. Anal. Calcd for $\mathrm{C_{10}H_8O_5S}$: C, 50.00; H, 3.36; S, 13.35. Found: C, 49.73; H, 3.35; S, 13.34. IR (KBr): 1740, 1671 $\mathrm{cm^{-1}}$. ^{1}H NMR (acetone-d_6): 8.264 (d, $J = 8.0$ Hz, 1H), 8.115 (d, $J = 8.0$ Hz, 1H), 7.931 (t, 1H), 7.700 (t, 1H), 6.715 (d, $J = 10.8$ Hz, 1H), 6.338 (d, $J = 10.4$ Hz, 1H) ^{13}C NMR (acetone-d_6): 167.42 (quat), 165.89 (quat), 150.21 (quat), 148.04 (CH), 134.43 (CH), 131.67 (CH), 131.20 (CH), 129.28 (quat), 127.51 (CH), 125.27 (CH).

2-Mercapto-5-methylbenzoic Acid, 8. This compound was prepared by the method of Allen and MacKay[6] in 33% yield after recrystallization from glacial acetic acid, mp 155−156 °C (lit.[7] 155−157 °C). IR (KBr): 1679 $\mathrm{cm^{-1}}$. ^{1}H NMR (acetone-d_6): 7.892 (s, 1H), 7.367 (d, $J = 5.0$ Hz, 1H), 7.251 (d, $J = 5.0$ Hz, 1H), 5.066 (s, 1H, SH), 2.328 (s, 3H). ^{13}C NMR (acetone-d_6): 168.24 (quat), 135.93 (quat), 135.21 (quat), 134.36 (CH), 132.99 (CH), 131.67 (CH), 126.69 (quat), 20.54 ($\mathrm{CH_3}$).

2-(2-Carboxyphenylthio)-5-methylbenzoic Acid, 9. This compound was prepared by a modification of the method of Protiva.[8,9] A mixture of 8.41 g (50.0 mmol) of **8**, 12.5 g (49.4 mmol) of 2-iodobenzoic acid, 15.0 g of 85% KOH (228 mmol), and 0.505 g (7.95 mmol) of copper powder in 125 mL of water was refluxed 8 h, cooled to room temperature, and filtered. The filtrate was acidified with HCl, and the resulting precipitate was filtered and washed twice with water. Recrystallization from glacial acetic acid afforded 7.55 g of diacid **9** (53.0% yield), mp 203−204 °C. IR (KBr): 1699, 1676, 1559 $\mathrm{cm^{-1}}$. ^{1}H NMR (acetone-d_6): 7.949 (d, $J = 7.8$ Hz, 1H), 7.731 (s, 1H), 7.432−7.271 (m. 3H), 7.205 (d, $J = 8.0$ Hz, 1H), 7.045 (d, $J = 7.8$ Hz, 1H), 2.383 (s, 3H) ^{13}C NMR (acetone-d_6): 168.04 (quat), 167.77 (quat), 140.88 (quat), 138.71 (quat), 135.12 (CH), 133.67 (CH), 133.41 (quat), 132.91 (CH), 131.85 (CH), 131.69 (CH), 131.57 (quat), 131.45 (CH), 126.67 (CH), 20.82 ($\mathrm{CH_3}$).

2,1-Benzoxathiol-3-one-1-spiro-1′-(5′-methyl-2′,1′-benzoxathiol-3-one), 5. This compound was prepared following the method of Lam and Martin.[10] In a $\mathrm{N_2}$-filled glovebox, a solution of 285 mg (0.990 mmol) of **9** in 2.00 g (25.3 mmol) of dry pyridine was treated gradually with 108 mg (0.995 mmol) of *tert*-butyl hypochlorite. After 5 min, the precipitate was vacuum filtered, washed with 20 mL of dry pentane, and vacuum-dried. The solid was stirred 20 min in boiling dried

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toluene and hot-filtered, and the filtrate was cooled in the refrigerator. The resulting solid was collected by vacuum filtration, 78 mg, 48% yield. mp 264−266 °C. Anal. Calcd for $C_{15}H_{10}O_4S$: C, 62.93; H, 3.52; S, 11.20. Found: C, 63.06; H, 3.39; S, 11.31. IR (KBr): 1736, 1722 cm^{-1}. ^1H NMR (acetone-d_6): 8.158−8.087 (m, 2H), 7.996−7.923 (m, 4H), 7.766 (d, J = 8.4 Hz), 1H), 2.517 (s, 3H) ^{13}C NMR (acetone-d_6): 167.41 (quat), 146,52 (quat), 142.87 (quat), 139.54 (quat), 137.93 (CH), 136.49 (CH), 134.96 (CH), 130.72 (quat), 130.63 (quat), 129.82 (CH), 129.58 (CH), 129.05 (CH), 128.84 (CH), 21.14 (CH_3) ^{17}O NMR (59.4 MHz, CH_2Cl_2): 325 (C═O), 270 (−O−).

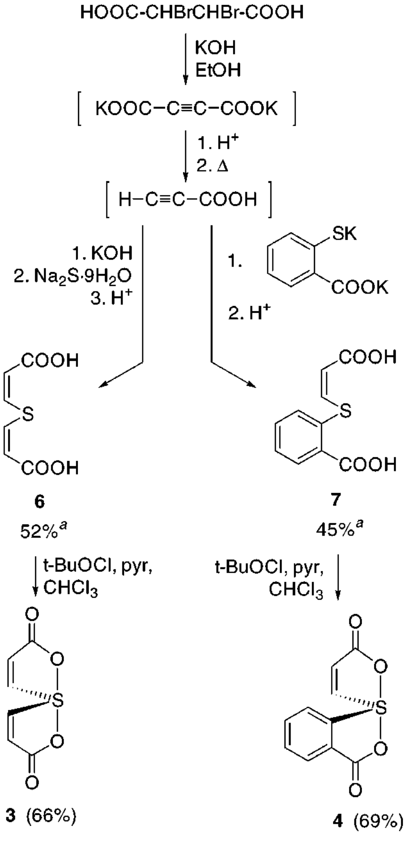
2-(2-Carboxyphenylsulfinyl)-5-methylbenzoic Acid, 12. Sulfurane **5** (100 mg) was dissolved in 50 mL of boiling acetone. After stirring 4 d in air, the solvent was removed on the rotary evaporator, and the residue was dried on the vacuum line. Attempts to determine the mp were frustrated by the dehydration of **12** to sulfurane **5** in the mp capillary. IR (KBr): 1717, 1690 cm^{-1}. ^1H NMR (acetone-d_6): 7.990 (d, J = 7.6 Hz, 1H), 7.875 (d, J = 8.0 Hz, 1H), 7.787 (s, 1H), 7.743 (t, 1H), 7.682 (d, J = 8.0 Hz, 1H), 7.582 (t, 1H), 7.525 (d, J = 8.0 Hz, 1H), 2.400 (s, 3H) ^{13}C NMR (acetone-d_6): 166.86 (quat), 166.73 (quat), 150.27 (quat), 146.90 (quat), 134.24 (CH), 133.75 (CH), 131.63 (CH), 130.96 (CH), 130.53 (CH), 130.37 (quat), 127.57 (CH), 127.28 (CH), 20.98 (CH_3).

Serendipitous Synthesis of (*E,Z*)-3,3′-Sulfinyldi(propenoic acid), 13. A vial containing a methanol solution of *Z,Z* sulfoxide diacid **10** was covered completely with aluminum foil, a tiny pinhole was made in the foil to allow very slow escape of the solvent, and the vial was allowed to stand. After roughly 50 days, the vial contained a small amount of methanol and some crystals, which were subsequently shown by X-ray crystallography to be **13**.[11] IR (KBr): 3057, 1709, 1664, 1614 cm^{-1}. ^1H NMR (acetone-d_6): 7.830 (d, J = 15.0 Hz, 1H), 6.782 (d, J = 10.0 Hz, 1H), 6.514 (d, J = 15.0 Hz, 1H), 6.500 (d, J = 9.8 Hz, 1H).

(*E*)-3-(2-Carboxyphenylsulfinyl)-2-propenoic Acid, 15. Sulfoxide diacid **11** (32.0 mg, 0.133 mmol) was dissolved in a mixture of 5 mL of water and 10 mL of methanol and kept 15 d in a closed container. Removal of solvent afforded 31.8 mg of **15**, 99.4% yield. mp 219−220 °C. IR (KBr): 1709, 1681 cm^{-1}. ^1H NMR (acetone-d_6): 8.183 (d, J = 7.75 Hz, 1H), 8.096 (d, J = 8.0 Hz, 1H), 8.037 (d, J = 15.0 Hz, 1H), 7.935 (t, 1H), 7.714 (t, 1H), 6.555 (d, J = 15.0 Hz, 1H) ^{13}C NMR (acetone-d_6): 167.48 (quat), 165.05 (quat), 153.39 (CH), 147.89 (quat), 135.36 (CH), 132.00 (CH), 131.55 (CH), 124.75 (CH), 124.31 (CH), 124.24 (quat).

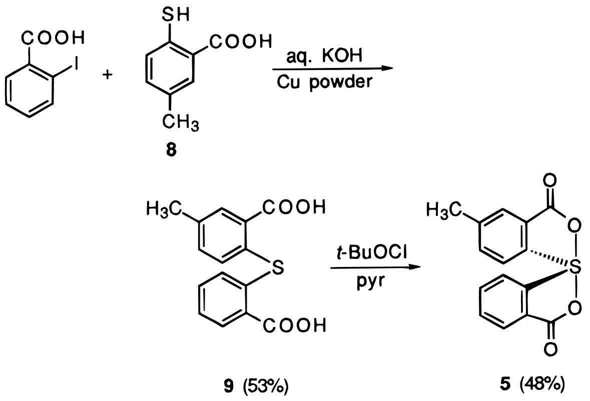
Kinetics of Hydrolysis of Sulfuranes. Two sulfuranes were dissolved in an NMR tube in 10:1 (v/v) acetone-d_6:DMSO-d_6. No procedures for drying the solvents were used. Since the HDO peak in the ^1H NMR spectrum was much larger than any sulfurane signal (typically by a factor of 7 or more), and since that implies that an even larger amount of D_2O was present, no extra water was required to obtain an excess concentration of water. The NMR probe was maintained at 40 ± 1 °C by the NMR hardware. Precise timing of data collection was provided by a short program written locally. An internal standard (anisole for **4** vs **5**; 1,1,2,2-tetrachloroethane for **3** vs **5**) was included. Hydrolyses were followed for roughly 2.5 half-lives, typically, and first-order treatment of the data yielded satisfactory linear plots. For **5**, the loss of the methyl signal vs an anisole aromatic signal at 6.90 ppm was followed. For **4**, the loss of the olefinic signal at 7.15 ppm vs the same anisole signal was followed. In the case of **3** vs **5**, both olefinic signals of **3** were unusable because of overlap with aromatic signals of other species. Therefore, from the $t = \infty$ signal intensity of product **10** was subtracted the signal (6.41 ppm) intensity of **10** at each time to give the intensity of **3** at each time. Similarly the methyl signal intensity of **12** at each time was subtracted from the methyl signal intensity of **12** at $t = \infty$ to give the intensity of **5** at each time. As a check, the loss of signal intensity of **5** as a function of time was used to calculate a rate constant, which was identical within experimental error to that calculated from the growth of product **12**. Two kinetic runs were made in the **3** vs **5** case. Three runs were made in the **4** vs **5** case.

Scheme 1



[a] from dibromosuccinic acid

Scheme 2



Results

Sulfuranes **3**−**5** were synthesized as shown in Schemes 1 and 2. Yields of sulfide diacids **6** and **7**, 52% and 45%, respectively, each reflect the overall yield of three steps done in one pot, since propiolic acid was not isolated.[12] It was found that good temperature control during the final acidification procedure leading to either **6** or **7** was essential to avoid cis−trans isomerization; 5−10% of the undesired trans isomer was produced if acid were added too quickly.

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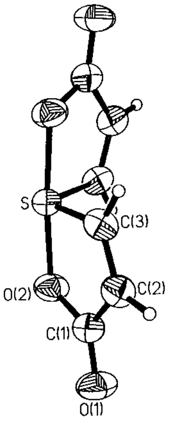
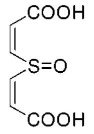


Figure 1. Structure of **3** as determined by X-ray crystallography. A C_2 axis passes through S, bisecting both the O−S−O bond angle and the C−S−C bond angle.

The ^{1}H NMR cis-coupling constant across an endocyclic carbon−carbon double bond is known to change as a function of ring size; in particular the cis-coupling in cyclopentene is 5.1 Hz[13] or 5.4 Hz.[14] It was found that the cis-couplings in **3** and **4** were 5.2 and 5.3 Hz, respectively, as compared to over 10 Hz for their precursors **6** and **7**, and over 10 Hz for their hydrolysis products **10** and **11**. Therefore, in the oxidations leading to **3** or **4**, cyclization to the desired sulfuranes could be quickly verified by ^{1}H NMR.

Products of hydrolysis of **3**, **4**, and **5**, namely **10**, **11**, and **12**, were obtained quantitatively by stirring an acetone solution of the appropriate sulfurane several days in air. In attempting to determine the mp of **12**, dehydration, presumably to sulfurane **5**, was noted. This was verified on a larger scale by heating **12** to 195−210 °C for 12 h in a closed flask evacuated to 0.2 Torr. A quantitative yield of sulfurane **5** was obtained.

Hydrolysis at 40 °C of solutions containing pairs of the sulfuranes (**3** and **5**, or **4** and **5**) was followed by ^{1}H NMR. Ratios of pseudo-first-order rate constants were: $k_3/k_5 = 8.20 \pm 0.24$; $k_4/k_5 = 1.79 \pm 0.13$.



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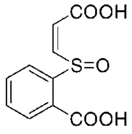

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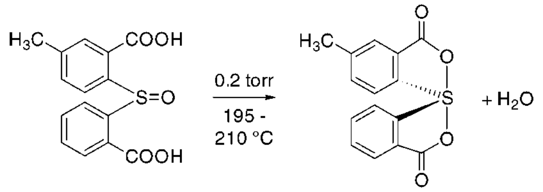
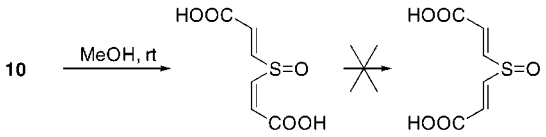


12

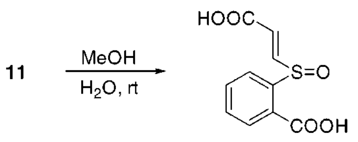
5 (~100%)

X-ray crystallographic structure determinations were carried out on sulfide diacid **7**, sulfurane **3**, and sulfurane **4**. Figure 1 shows an ORTEP plot of the structure of **3**. Important geometrical parameters from these determinations are presented in Table 1. In **3**, a 2-fold axis passes through sulfur normal to the O−S−O bond and bisecting the C−S−C bond angle, so that a = g, b = h, and so on.

In preparing a sample of sulfoxide diacid **10** for X-ray crystallography, it was found that slow evaporation of a methanol solution of **10** gave crystals of the isomeric **13**. The *E*,*E* isomer, **14**, was not detected. The isomerization of **10** to **13** was studied by ^{1}H NMR and a rate constant of $5.8 \pm 0.1 \times 10^{-7}$ s^{-1} was determined. It was found that sulfoxide acid **11** in methanol underwent an analogous isomerization at room temperature, with $k = 5.2 \pm 0.1$ $\times$ 10−7 s^{-1}.



13 **14**



15

Samples of **10** protected from light isomerized at the same rate as did samples of **10** exposed to ambient daylight. Under conditions sufficient to isomerize **10** or **11**, **6** and **7** were unchanged. A sample of **6** in methanol containing DMSO did not undergo isomerization. A sample of **10** in methanol containing a trace of HCl gave a product mixture having an extremely complicated ^{1}H NMR spectrum; over 40 peaks were noted. A sample of **11** containing about 10 mol % KOH in methanol-d_4 isomerized with a rate constant of $1.0 \pm 0.1 \times 10^{-6}$ s^{-1}. The rate constants for the isomerization of **11** in several solvents were measured: rate constants (relative to that in methanol) were D_2O:DMSO-d_6:CD_3OD:acetone-d_6 3.9:1.5:1.0:0.2. (The rate in acetone solvent was inconveniently slow, so the rate constant is an estimate based on the observation of 25% isomerization after 40 days).

^{17}O NMR spectra of sulfuranes **3**, **4**, and **5** are reported in Chart 1, along with ^{17}O data for other hypervalent molecules and nonhypervalent reference compounds.

Discussion

Benzoannelation imparts kinetic stability to sulfuranes: **3**, lacking phenyls, hydrolyzes 8.2 times faster than **5**, having two phenyls. It is salutary to note that the factor of 8.2 is quite small. By comparison, the “five-membered ring effect”, another Martin design feature, produces kinetic stabilization of at least several orders of magnitude.[15]

To adequately interpret this subtle rate enhancement, one should be able to write the rate-determining-step (rds), one should have structural data pertinent to all species involved in the rds, and one should have data which would permit one to disentangle any solvent effect. (Even though the solvent used was identical for **3** and **5**, it is possible that differences in solvation of **3** and **5** and of intermediates derived from them might account for a

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(13) Smith, G. V.; Kriloff, H. *J. Am. Chem. Soc.* **1963**, *85*, 2016−2017.

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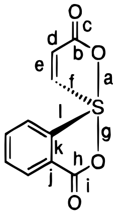
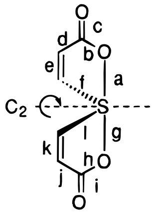
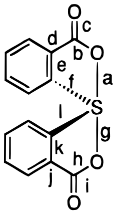
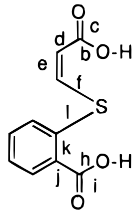
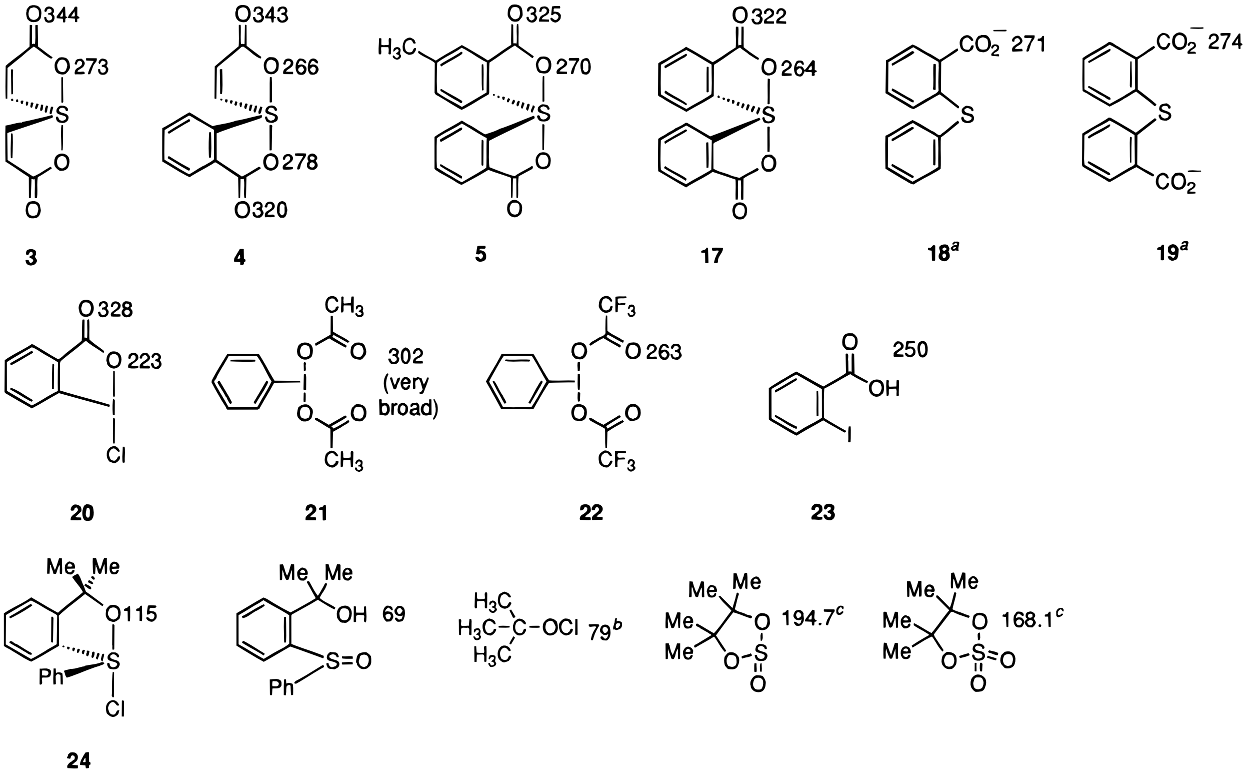
Table 1. Comparison of Sulfurane Structural Parameters from X-Ray Crystallography

 **4**[a]		 **3**[a]	 **17**[b]	 **7**[a]	
a 1.826(5)	g 1.856(5)	a 1.839(2)	a 1.83(1)		
b 1.340(8)	h 1.328(8)	b 1.331(3)	b 1.34(3)	b 1.319(4)	h 1.315(4)
c 1.206(9)	i 1.191(9)	c 1.200(3)	c 1.21(3)	c 1.225(4)	i 1.220(4)
d 1.456(9)	j 1.494(9)	d 1.470(4)	d 1.46(3)	d 1.440(5)	j 1.485(5)
e 1.321(9)	k 1.371(9)	e 1.309(3)	e 1.44(3)	e 1.335(4)	k 1.395(4)
f 1.767(7)	l 1.787(6)	f 1.770(3)	f 1.82(2)	f 1.721(3)	l 1.789(3)
ab 112.7(4)	gh 109.6(6)	ab 113.4(2)	ab 114.5[c]		
bc 121.4(6)	hi 124.2(7)	bc 123.1(3)	bc —[d]	bc 122.0(3)	hi 122.7(3)
cd 127.4(6)	ij 126.2(6)	cd 126.5(3)	cd —[d]	cd 122.6(3)	ij 123.3(3)
bd 111.2(6)	hj 109.6(6)	bd 110.4(2)	bd 112.5[c]	bd 115.3(3)	hj 113.9(3)
de 114.5(6)	jk 114.7(6)	de 115.0(2)	de 113.1[c]	de 124.1(3)	jk 122.5(3)
ef 113.6(5)	kl 112.9(5)	ef 113.9(2)	ef 110.4[c]	ef 127.3(3)	kl 120.5(2)
ag 175.2(2)		ag 174.9(1)	ag 178.5[c]		
fl 106.8(3)		fl 105.3(2)	fl 107.8[c]	fl 100.3(2)	

[a] This work [b] Ref. 18 [c] Esds varied between 0.7 and 2.2° [d] Not reported

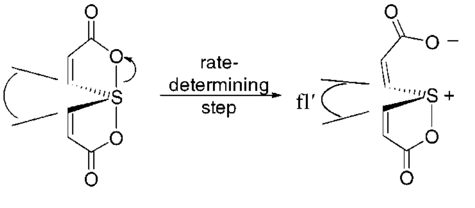
Chart 1. ^{17}O NMR Chemical Shifts



[a] pyridine solvent, T = 80 °C [b] Sugawara, T.; Kawada, Y.; Katoh, M.; Iwamura, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3391-3396. [c] Hellier, D. G.; Liddy, H. G. *Magn. Reson. Chem.* **1988**, *26*, 671-674.

nontrivial portion of such a small kinetic effect). We do not profess to have met all these requirements. Nevertheless, we offer the following thoughts.

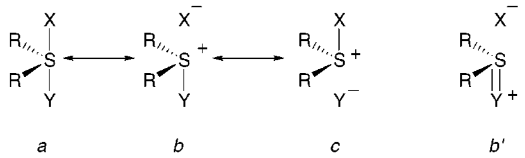
On the basis of numerous mechanistic studies of hydrolyses of sulfuranes structurally similar to those under discussion here,[2,16] it is reasonable to take the heterolysis of the axial S—O bond to be the rds, as shown below for **3**. We focus on the so-called equatorial angle, which is labeled "fl" in Table 1. Structural studies of sulfonium salts would suggest the C—S—C angle in **16** is smaller than its value in **3**.[17] Similarly, the C—S—C angle in the sulfonium carboxylate resulting from heterolysis of **5** would be smaller than the equatorial angle of **5**. That is, the rate-determining step probably involves a contraction of the equatorial angle. If this is indeed the case, a "least-motion" argument can explain our kinetic results for **3** and **5**.



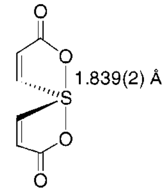
3 **16**

The equatorial angle of **3** is 105.3(2)°. The equatorial angle of **5** is not known but should be nearly identical to that of sulfurane **17**, which is simply **5** lacking the methyl group. The X-ray data for **17** are of poor quality, unfortunately, (R = 0.146 (observed), R = 0.172 (all)) owing to difficulty in obtaining a well-shaped crystal.[18] The reported equatorial angle for **17** is 107.8°. This is consistent with well-measured equatorial angles reported for other spirobicyclic dioxasulfuranes having two equatorial phenyls (108.1(4)°,[19] 107.6(3)°,[19] 107.9(1)°,[20] 112.4(1)°[21]). Even with the worst esd reported for **17**, 2.2°, the equatorial angle of **17** (and, by extension, **5**) is larger than that of **3**. The least motion argument posits that **3**, having a smaller equatorial angle contraction to undergo than does **5**, would undergo the rds faster than **5**.

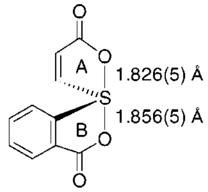
The kinetic behavior of the intermediate case, **4**, having one phenyl, does not fall at the midpoint, which would be hydrolysis 4.1 times faster than **5**. Rather, **4** is more kinetically stable; namely, only 1.8 times the hydrolysis rate of **5**. This is congruent with earlier ab initio calculations which found sulfuranes R_2SXY with nonidentical axial ligands (X, Y) are thermodynamically more stable than the average of the thermodynamic stabilities of the two relevant symmetrical sulfuranes, R_2SX_2 and R_2SY_2.[22] We proceed with caution since calculations of thermodynamic stability of a reactant may not suffice to explain its kinetic behavior. The explanation advanced to rationalize the calculations was that to take energetic advantage of a charge-separated resonance structure, b or c, one axial ligand should be particularly capable of accommodating negative charge, and the other should be particularly capable of stabilizing an adjacent sulfonium center, conceivably via resonance structure b′.



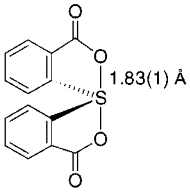
It is more reasonable to meet these disparate requirements with two different axial ligands rather than to expect two of the same ligand to do both jobs. If, for example, X were the ligand which was better suited to excess electron density and Y were the ligand suited to stabilization of an adjacent sulfonium ion center, which is to say resonance structure b were quite important, and c not so, then, reasoning from b and b′,[23] one predicts that the S−X bond in unsymmetrical sulfurane R_2SXY should be longer than the S−X bond in symmetrical sulfurane R_2SX_2, and the S−Y bond in unsymmetrical sulfurane R_2SXY should be shorter than the S−Y bond in symmetrical sulfurane R_2SY_2. In the present case, it is clear from examining the S−O bond lengths that in **4** the carboxylate group of the benzoannelated five-membered ring (hereinafter the B (for "benzoate") ring) is the ligand which assumes the role of accommodating negative charge and the carboxylate of the nonbenzoannelated five-membered ring (hereinafter the A (for "acrylate") ring) is the ligand which is better able to stabilize the partially positive sulfur. This conclusion may be restated more simply in terms of resonance structures: **4b** is more important than **4c**.



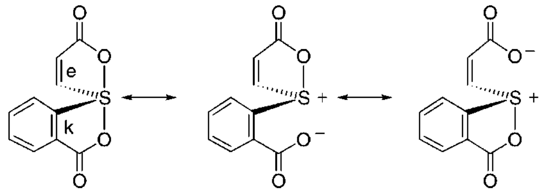
3



4



17



4a **4b** **4c**

An alternative argument is as follows: since a carbon−carbon double is shorter than a benzene carbon−carbon bond (e.g., in **4**, bond e, 1.321(9) Å, is shorter than bond k, 1.371(9) Å), the shorter S−O bond in the A ring and the longer S−O bond in the B ring are merely structural consequences of carbon−carbon bond lengths in their respective rings. However, this line of reasoning would predict a "short" S−O bond in **3**, contrary to fact (in **3**, e is 1.309(3) Å but S−O is 1.839(2) Å).

If **4b** is more important than **4c**, one might expect a lower carbonyl stretching frequency in the B ring than in the A.[24] Unfortunately, only a broad signal at 1715 cm^{-1} was observed in the IR spectrum of **4**, so this prediction cannot be checked.

The least-motion argument involving contraction of the equatorial angle, which was suggested as an explanation of the relative reactivity of **3** and **5**, is not invalidated by

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(16) (a) Kapovits, I.; Rábai, J.; Ruff, F.; Kucsman, Á.; Tanács, B. *Tetrahedron* **1979**, *35*, 1875−1881. (b) Vass, E.; Ruff, F.; Kapovits, I.; Rábai, J.; Szabó, D. *J. Chem. Soc., Perkin Trans. 2* **1993**, 855−859. (c) Vass, E.; Ruff, F.; Kapovits, I.; Szabó, D.; Kucsman, Á. *Ibid.* **1997**, 2061−2068. (d) Ádam, T.; Ruff, F.; Kapovits, I.; Szabó, D.; Kucsman, Á. *Ibid.* **1998**, 1269−1275.

(17) Perozzi, E. F.; Paul, I. C. In *The Chemistry of the Sulphonium Group*; Stirling, C. J. M., Patai, S., Eds.; Wiley: London, 1981; pp 15−77.

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(21) Lam, W. Y.; Duesler, E. N.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 127−135.

(22) Eggers, M. D.; Livant, P. D.; McKee, M. L. *J. Mol. Struct. (THEOCHEM)* **1989**, *186*, 69−84.

(23) Livant, P. *J. Org. Chem.* **1986**, *51*, 5384−5389.

(24) Livant, P.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 5761−5767.

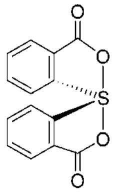
including in the comparison the equatorial angle of **4**, 106.8(3)°. This value is between the 105.3(2)° for **3** and the 107.8° for **5**'s model, **17**, and the reactivity of **4** is between that of **3** and **5**.

^{17}O NMR Spectra. Although our synthesis of nonbenzoannelated sulfuranes **3** and **4** enabled us to quantify the importance of benzoannelation in sulfurane design, the original goal of increasing tumbling rate to produce observable ^{17}O NMR lines was rendered moot by our observation that ^{17}O NMR spectra which were unobservable in hot acetonitrile or toluene solvent were observable using room-temperature dry methylene chloride. We were at a loss to explain the improvement since the viscosities of acetonitrile and methylene chloride are not so different (CH_2Cl_2: 0.393 cP at 30 °C; CH_3CN: 0.345 cP at 25 °C),[25] but welcomed the good fortune and undertook a study of various hypervalent systems of interest to us (see Chart 1).

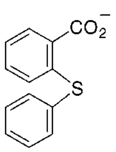
^{17}O NMR chemical shifts have a diamagnetic and a paramagnetic component, with the paramagnetic term providing the bulk of the variation of chemical shifts within a given class of compounds.[26] The diamagnetic term is important when comparing compounds in which different nuclei are bonded to oxygen, for example water vs dimethyl ether.

The paramagnetic term has three important components, according to the well-known Karplus–Pople equation: (i) $(\Delta E)^{-1}$ term, in which ΔE is an average electronic excitation energy, sometimes approximated using the first band in the electronic spectrum, (ii) $\langle r^{-3}\rangle_{2p}$, a p-orbital "size" term, and (iii) Q_{AA} and Q_{AB} (A = oxygen, B = neighboring atom), which, roughly speaking, include the "charge" on oxygen and the 2p–2p π bond order between oxygen and its neighbor(s). This final component has been illustrated[27] by comparing the ^{17}O chemical shifts of acetone (569 ppm) and protonated acetone (310 ppm). The former has an "undiluted" π bond and is thus shifted far downfield. The latter may be viewed as a resonance hybrid of a double-bonded form (chemical shift like that of acetone) and a single-bonded form (chemical shift like that of 2-propanol, 38 ppm).[28] The shift of 310 ppm is then an approximate average of 569 and 38 ppm.

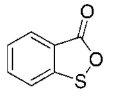
Might a similar consideration of π bond orders suffice to explain the shifts observed for **3**, **4**, and **5** (and **17**)? Earlier work on carbonyl stretching frequencies in sulfuranes[24] showed quite a significant contribution of carboxylate anion resonance forms in carboxy sulfuranes and thus might serve as a guide for π-bond order. For example, the 1724 cm^{-1} frequency observed for **17** lies between the 1609 cm^{-1} for **18** (full carboxylate anion character; low π-bond order) and the 1790 cm^{-1} for **26** ("no" carboxylate anion character; high π-bond order).[29] Similarly, the ^{17}O chemical shift of the carbonyl oxygen of **5** should lie between that of **18** and **26**, if the π-bond order effect were the dominant effect on the chemical shift. Unfortunately, the carbonyl ^{17}O chemical shift of **26** is unknown, and would be difficult to measure because **26** is thermally unstable. A proper "substitute" for **26** in this comparison would be a carbonyl compound having a carbonyl stretching frequency close to that of **26** and whose carbonyl ^{17}O chemical shift is known. Benzoyl chloride (1763 cm^{-1})[30] or benzoyl peroxide (1792 and 1772 cm^{-1})[31] suggest themselves. The ^{17}O NMR spectrum of benzoyl peroxide (BPO) has not been reported; therefore we measured it. It consists of a single broad signal ($W_{1/2} \approx 700$ Hz) at 340 ppm (CH_2Cl_2 solvent). The absence of two signals suggests the operation of some type of exchange process, conceivably involving impurities. The spectrum was identical whether BPO was taken directly from the jar or whether it was freshly recrystallized, so impurities would seem not to be the culprit. Oxygen scrambling processes in diacyl peroxides are known,[32] but occur on a much longer time scale, or not at all.[33] Another possible explanation is that the rotational correlation times of the two types of oxygens are sufficiently different that one type is observable, but the other is so broadened that it is unobservable. For the sake of logical completeness, it should be noted that it is possible (but unlikely) that BPO's carbonyl oxygen and peroxide oxygen have the same chemical shift. In any event, benzoyl peroxide's one signal at 340 ppm is a mystery. Therefore, benzoyl chloride by default may be considered as a substitute for **26**. Its one signal at 483 ppm is unambiguously due to the carbonyl oxygen. This fits in with the carbonyl ^{17}O signal of **5** (325 ppm) lying between that of a model compound possessing low π-bond order (**18**, 271 ppm) and that of one possessing high π-bond order (PhCOCl, 483 ppm).



17
1724 cm^{-1}



18
1609 cm^{-1}



26
1790 cm^{-1}

The carbonyl oxygens of **4** absorb at 343 and 320 ppm. Our assignment of the 343 ppm signal to the A-ring carbonyl of **4** and the 320 ppm signal to the B-ring carbonyl is based on the similarity of these chemical shifts to those of **3** (344 ppm) and **5** (325 ppm) (or **17**, 322 ppm), respectively. Assuming these assignments are correct, we may state that the A-ring carbonyl has higher π-bond order than the B-ring carbonyl, which in turn means that the carboxyl group in the A-ring has less carboxylate anion character than the carboxyl group in the B-ring, or, as was stated before, resonance structure **4b** is more important than resonance structure **4c**. Therefore, the conclusion based on ^{17}O NMR chemical shifts is consistent with the conclusion based on axial bond lengths. It should be noted that a single crystal is not required for NMR spectroscopy, and the unmistakable 20 ppm difference in chemical shifts produced by

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(25) *Handbook of Chemistry and Physics*, 48th ed.; Weast, R. C., Ed.; Chemical Rubber Co.: Cleveland, 1967–68; pp F35–F40.

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(33) Greene, F. D. *J. Am. Chem. Soc.* **1959**, *81*, 1503–1506.

two carbonyls even as similar as the A-ring carbonyl of **4** and the B-ring carbonyl of **4** recommends ^{17}O NMR spectroscopy as a sensitive tool for investigating other oxygen-containing hypervalent systems.

Some exploratory results are presented in Chart 1. Compounds **20**−**22** are iodinanes (10-I-3 species) which have at least one carboxyl ligand. Chloroiodinane **20** exhibits a carbonyl oxygen absorption at 328 ppm, which is quite similar to the carbonyl absorptions of sulfuranes **5** and **17**. This may be fortuitous. The “ether” oxygen of **20** is shielded relative to those of **5** and **17** by 41−47 ppm. Part of this may be a bond angle dependence. Because of the larger covalent radius of iodine, the ether oxygen of **20** must have a larger bond angle than the ether oxygen of **5** or **17**. This would produce an upfield shift (cf. ether oxygen of γ-butyrolactone, 178.5 ppm vs that of δ-valerolactone, 166.5 ppm).[34] The remainder of the difference is probably a consequence of the diamagnetic term (e.g. ClO_3^- 297 ppm vs IO_3^- 206 ppm).[35] Iodinanes **21** and **22** each exhibit only one oxygen absorption, unexpectedly. The peak for **21** is quite broad, but the one for **22** is sharp, by ^{17}O standards. We cannot at present offer a good explanation of these spectra; they are included in the hope that others with greater expertise will be motivated to propose an explanation. The crystal structures of iodoarene dicarboxylates usually show significant “nonbonded” contacts between carbonyl oxygen and iodine, either intra- or intermolecularly.[36] It is therefore not unreasonable to consider the possibility of degenerate [1,3] sigmatropic shifts of iodine from −O− to =O as a route to oxygen scrambling. Another possible route to oxygen scrambling is dissociation to an iodonium cation carboxylate anion pair followed by I−O bond formation. However, we have no data to support or refute either of these suggestions.

The ^{17}O chemical shift of chlorosulfurane **24**, 115 ppm, is in a sparsely populated region of the chemical shift range. It is difficult to find a compound with which to compare **24**. Dimethyl sulfite (−O−) happens to absorb at 115 ppm too,[28] but this may be misleading since the oxygen in **24** is attached to a tertiary carbon. Compare the chemical shifts of methanol (−37 ppm) and 2-(2-phenylsulfinyl)phenyl)-2-propanol (69 ppm), a difference of over 100 ppm. A better comparison might be tetramethylethylene sulfate (−O− 168.1)[37] or tetramethylethylene sulfite (−O− 194.7 ppm).[37] It is then difficult to rationalize the “shift” from 168.1 or 194.7 ppm to 115 ppm. A possible explanation may involve a bond angle change. Comparing ethylene sulfite (−O− 155.5 ppm) to trimethylene sulfite (−O− 126.1 ppm) to tetramethylene sulfite (−O− 145.0 ppm) shows that geometry changes can sometimes have a large effect.[37] The C−O−S bond angle in **24** is 115.9(2)°.[23] It is also possible to argue the sulfur to which the oxygen in **24** is bonded is so dissimilar to either a sulfite sulfur or a sulfate sulfur that any comparison of sulfurane **24** to either a sulfite or a sulfate is invalid.

Ab Initio Calculations of Sulfurane Structure. The theoretical description of hypervalent molecules in general and sulfuranes in particular is a problem of long-standing interest to theoreticians.[38] Accurate calculations of sulfurane structure have been done most often for SF_4,[22,39] a small molecule with an experimental geometry available for comparison. However, we would argue that fluorine-containing systems, hypervalent or not, are inherently atypical due to the extreme electronegativity of fluorine. Further, “Martin-type” sulfuranes, which account for a large fraction of structurally well-characterized sulfuranes, do not resemble SF_4. Therefore, the ability of a theoretical method to provide accurate geometries of hypervalent sulfur species of practical interest to experimentalists might be more validly assessed using a test molecule other than SF_4. With the X-ray structure of **3** in hand, and noting that the number of atoms in **3** is fairly small, and that the C_2 symmetry axis reduces the size of the problem still further, we propose **3** as a more suitable test molecule with which to evaluate theoretical methods.

Acting on this suggestion, we carried out geometry optimizations of **3** using a wide variety of methods, including molecular mechanics, semiempirical, and ab initio calculations. Our purpose was to survey methods which could be of practical value in doing calculations on the larger molecules that experimentalists routinely synthesize and study. Accordingly, calculations employing very large basis sets and/or sophisticated correlation treatments were purposely excluded. All calculations were carried out using the SPARTAN 4.0 system of programs.[40] Johnson[41] has pointed out that DFT results are to an unfortunate extent a function of the details of implementation employed by the particular program. SPARTAN 4.0 uses numerical basis sets, with DN purported to be roughly equivalent to 6-31G and DN* to

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Chart 2. Bond Lengths of 3 Calculated by Various Methods

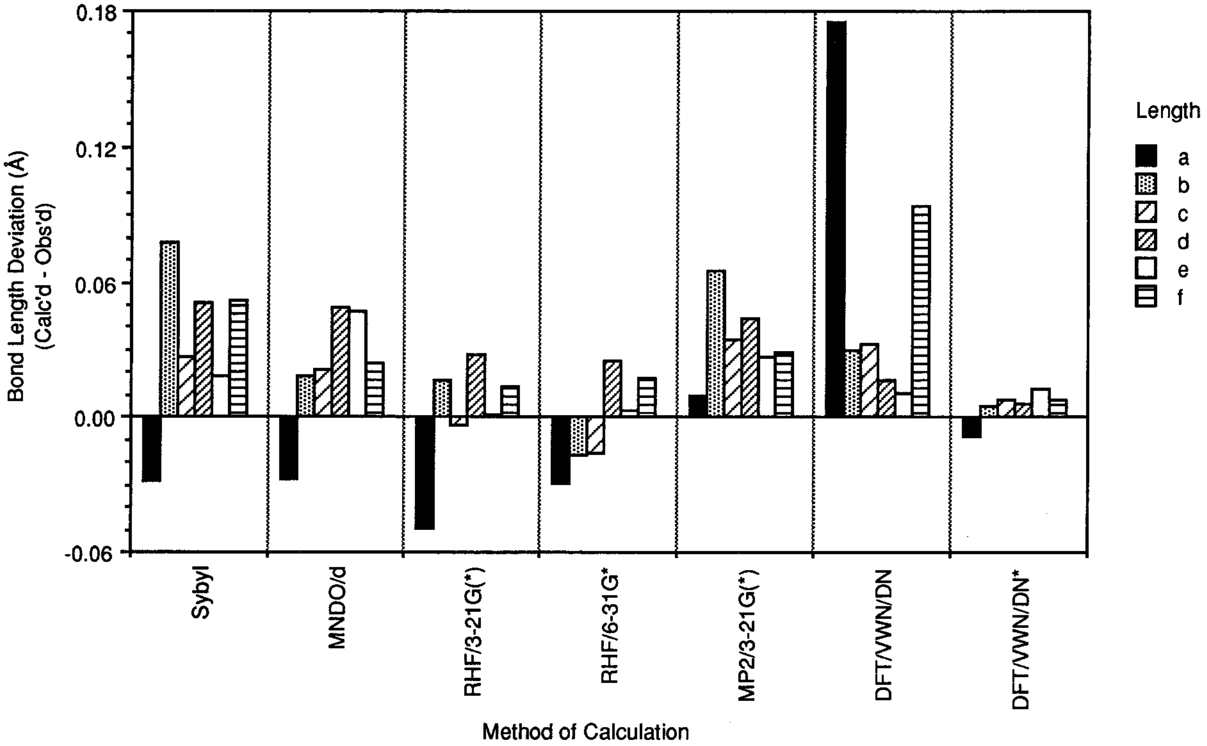
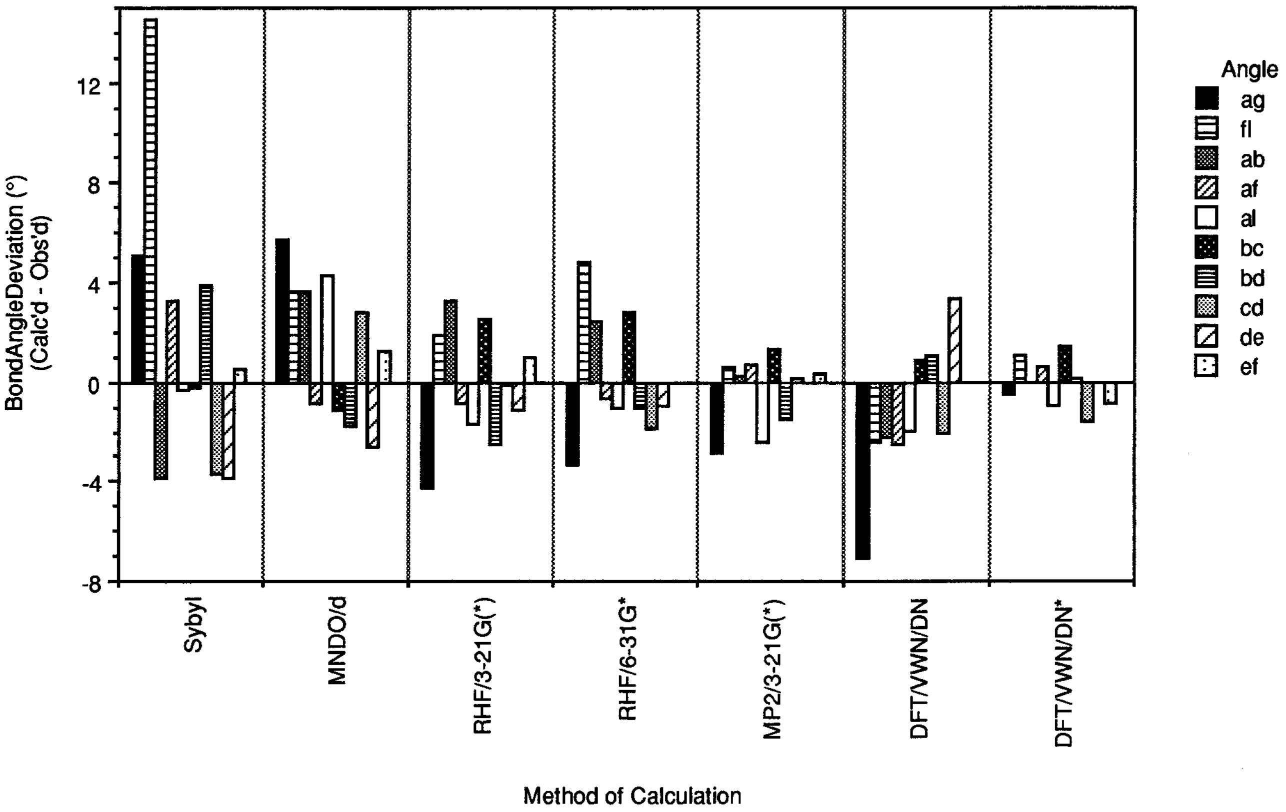


Chart 3. Bond Angles of 3 Calculated by Various Methods



6-31G*. The LSD approximation is used with the Vosko, Wilk, and Nusair (VWN) exchange-correlation functional.[42]

The only criterion upon which the calculations were judged was how well the calculated geometry agreed with the experimental geometry of **3**. The results are presented graphically in Charts **2** and **3**. The bond lengths and angles are named as in Table 1. In both charts, the left-to-right order of plotting within each group of bars is identical to the top-to-bottom order in the legend, and "deviation" means simply the calculated value minus the observed value.

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The three-center four-electron axial bond is at the heart of the structure of a trigonal bipyramidal hypervalent like **3**. This parameter, S−O bond length “a”, is the left-most bar in each group in Chart 2. Two other important parameters are the O−S−O angle (the arc of which passes between the two equatorial substituents), “ag”, and the C−S−C equatorial angle, “fl”, which are, respectively, the two left-most bars in each group in Chart 3.

Not surprisingly, molecular mechanics with the Sybyl force field was quite poor. Bond lengths were not as bad as with DFT/VWN/DN, but calculated bond angles were worthless. The calculated axial angle (“ag”) of 180.0° was unacceptable (cf. 174.9(1)° observed) and the equatorial angle (“fl”) of 119.88° (cf. 105.3(2)° observed) was worse than that. Also, it is fair to call the DFT treatment using the DN basis a crashing failure.

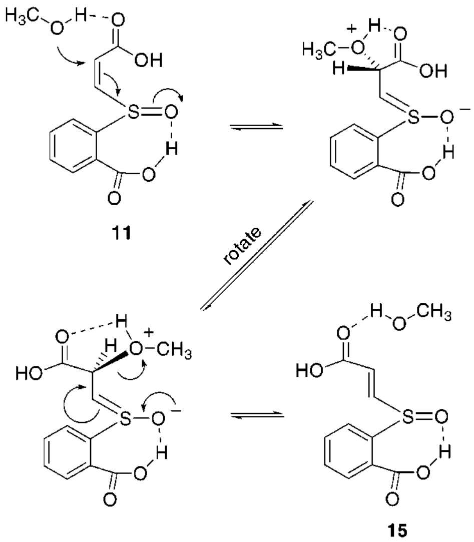
It was worrisome that MNDO/d, although acquitting itself respectably with regard to bond lengths, erred on the axial angle (“ag”) so much as to exceed 180° and render the sulfur slightly saddle-shaped.

The simple HF calculations using polarized basis sets, 3-21G(*) and 6-31G*, were very roughly similar. The axial length (“a”) was strongly underestimated using 3-21G(*), though. When a correlation treatment was included (MP2), it was anticipated that better geometries would be obtained. While the bond angles were clearly better, it was surprising to find the bond lengths had gotten worse. The rms bond length deviations for 3-21G(*), 6-31G*, and MP2/3-21G(*) were, respectively, 0.025, 0.020, and 0.039 Å. However MP2/3-21G(*) did a much better job on the axial length (“a”), a deviation of 0.0098 Å compared to −0.0498 Å and −0.0293 Å for 3-21G(*) and 6-31G*, respectively.

Clearly the method of choice, judging from these results, is DFT using a polarized basis (DFT/VWN/DN*). The rms bond length deviation was 0.008 Å and the rms bond angle deviation was 0.90°. Such a result is somewhat unexpected, since the VWN functional has been shown to perform much more poorly than several other functionals.[43]

Double Bond Isomerization. Sulfoxide diacid **10** isomerizes to **13** on standing in methanol. The double bond isomerization is very slow, having a half-life of about 14 days at room temperature. Sulfoxide acid **11** undergoes the same slow isomerization in methanol, with a half-life of about 15 days. Apparently, the sulfinyl group is required, as the analogous sulfide acids **6** and **7** did not undergo the isomerization. The sulfinyl group must be intramolecular, as **6** in methanol solvent containing dimethyl sulfoxide did not undergo the isomerization. The reaction changes when **10** in methanol is treated with a trace of acid. A large number of products are formed, many of which are methyl esters. No attempt was made to further characterize these products. The effect of base is to accelerate the isomerization rate constant by a modest factor of 1.7. A tentative mechanism consistent with these observations is presented in Scheme 3.

Scheme 3



In the case of **11**, there is only one double bond which may isomerize. In **10**, there are two, yet only one isomerizes. This raises the question of why the other double bond does not isomerize too. A plausible suggestion is that **10** has an internal hydrogen bond between sulfinyl oxygen and one carboxylic acid, as shown in Scheme 3. On conversion to **13**, this hydrogen bond may be retained and the lower energy of a trans double bond results in lower energy overall for **13** relative to **10**. However, for **13** to isomerize to **14**, the system must give up the intramolecular hydrogen bond to gain a trans double bond. Since the energy lowering of the cis−trans isomerization, typically less than 2 kcal/mol,[44] is much less than the bond energy of a hydrogen bond, roughly 5 kcal/mol,[45] the isomerization of **13** to **14** is unfavorable.

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Supporting Information Available: Additional details of crystallographic studies of **3**, **4**, and **7**, and Cartesian coordinates and final energies for all calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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