Synthesis and Carbon-13 Nuclear Magnetic Resonance Spectroscopy of 5,6-Dihydro-2-methyl-1,4-oxathiin, *trans*-Tetrahydro-1,4-benzoxathiin, 1,4-Tetrahydro-[9,10]benzoxathiin, the 4-Oxides, 4,4-Dioxides and Related Acyclic Compounds

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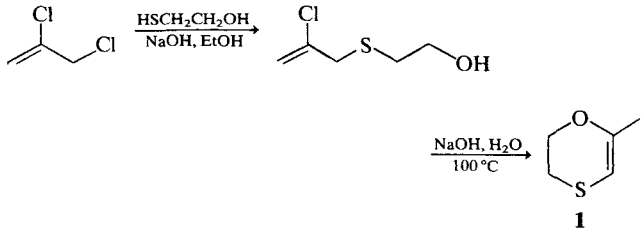
The results of a ^{13}C NMR spectral investigation involving 5,6-dihydro-1,4-oxathiins, 1,4-tetrahydro[9,10]benzoxathiin, *trans*-tetrahydro-1,4-benzoxathiin, and the corresponding sulfoxides and sulfones are reported. An interpretation involving a dipolar structure with $(2p\rightarrow 2p)\pi$ conjugation as opposed to $(2p\rightarrow 3d)\pi$ interactions with the vinyloxy sulfides seems consistent with trends in the ^{13}C NMR shifts. For the sulfoxides and sulfones, the substituent-induced chemical shift (SCS) effects at the β vinylic carbons (βSO and βSO_2 effects) are considerably less than those at sp^3 carbons. The γSO and γSO_2 values at the $sp^2\gamma$ carbons indicate *deshielding*, in contrast to the shielding at the sp^3 carbons.

INTRODUCTION

Various 5,6-dihydro-1,4-oxathiins (e.g. 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxamide[1]) and specific *S*-oxide derivatives (e.g. 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxamide 4,4-dioxide[1]) possess significant systemic fungicidal properties. Recently, considerable interest has focused on the syntheses and synthetic elaboration of other substituted 1,4-oxathiins[2] as well as 1,4-thiazine[3] and 1,4-dithiin analogues[3,4] in search of significant activity against various strains of bacteria, fungi and parasites. Although the value of ^{13}C NMR spectroscopy as applied to organic structure determinations is unquestioned,[5] there is surprisingly little correlative ^{13}C NMR information on substituted 1,4-oxathiins despite the large number of compounds having the 1,4-oxathiin structural skeleton. As new synthetic strategies provide access to previously unavailable 1,4-oxathiin analogues,[6] ^{13}C NMR parameters could be vital determinants in the confirmation of their structures. In this report, we describe the ^{13}C NMR spectra and 'substituent-induced chemical shifts' (SCS)[5] at sp^2 and sp^3 carbons in substituted 1,4-oxathiins resulting from conversion of sulfenyl sulfur to the sulfinyl and sulfonyl derivatives. (For a recent example of SCS effects, see Ref. 7.)

Syntheses

2-Mercaptoethanol in ethanolic sodium hydroxide was allowed to react with 2,3-dichloropropene to afford 2-(2-chloroallylthio)ethanol (69%) which cyclizes to 5,6-dihydro-2-methyl-1,4-oxathiin (**1**)[8] in the presence of sodium hydroxide (13% yield). 5,6-Dihydro-2-methyl-1,4-oxathiin can also be obtained from condensation of 2-hydroxy-ethanethiol and chloroacetone in refluxing methanolic sodium hydroxide, although the yield is not reported.[8b] Both 5,6-dihydro-2-methyl-1,4-oxathiin 4-oxide (**2**) and 5,6-dihydro-2-methyl-1,4-oxathiin 4,4-dioxide (**3**) were prepared by oxidation of **1** with one and two equivalents of *m*-chloroperoxybenzoic acid (*m*CPBA),[9] respectively.



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2-Mercaptoethanol was condensed with cyclohexanone in the presence of catalytic *p*-toluenesulfonic acid (*p*-TsOH) to give 2,2-hexamethylene-1,3-oxathiolane (43%). Oxidation of 2,2-hexamethylene-1,3-oxathiolane with one equivalent of *m*CPBA to the spiro 1,3-oxathiolane sulfoxide (92%), followed by azeotropic distillation (catalyzed by *p*-TsOH) gave 1,4-tetrahydro[9,10]benzoxathiin (**4**) in 29% yield.[2a,10] Oxidation of **4** with the appropriate equivalents of *m*CPBA afforded 1,4-tetrahydro[9,10]benzoxathiin 4-oxide (**5**) or 1,4-tetrahydro[9,10]benzoxathiin 4,4-dioxide (**6**),[2a,9] both of which were readily purified on alumina (column chromatography).

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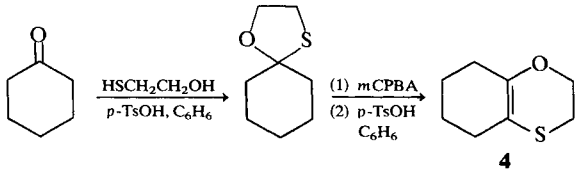


4

The preparation of *trans*-tetrahydro-1,4-benzoxathiin (**7**) has been described previously.[2a,9b] A 2:1 axial-equatorial ratio of diastereoisomeric sulfoxides [*trans*-tetrahydro-1,4-benzoxathiin 4-oxides (**8**, **9**)] was obtained by oxidation of sulfide **7** with one equivalent of *m*CPBA while *trans*-tetrahydro-1,4-benzoxathiin 4,4-dioxide (**10**) resulted from oxidation of **7** with two equivalents of *m*CPBA.[9]

Divinyl sulfide (**11**)[11] was obtained by base-catalyzed dehydration of 2,2'-thiodiethanol with potassium hydroxide at 200° while divinyl sulfoxide (**12**)[12] was prepared by oxidation of **11** with one equivalent of *m*CPBA. Divinyl sulfone (**13**) was obtained from Union Carbide and was distilled prior to use.

^{13}C NMR spectra

The ^{13}C NMR chemical shift assignments for all of the sp^3 hybridized carbons in compounds **1–10** (Table 1) were corroborated by comparison with the ^{13}C shifts of 1,4-oxathiane, *trans*-1,4-oxathiadecalin, the isomeric 4-oxides and the 4,4-dioxide.[13] The ^{13}C NMR chemical shifts of the vinylic carbons were assigned on the basis of anticipated inductive and resonance effects arising from oxygen[14a] and sulfur heteroatoms[14b] as well as the sulfinyl and sulfonyl moieties,[14b] in conjunction with the multiplicity of the carbon signals during coherent proton off-resonance decoupling experiments.[15]

^{13}C NMR Chemical shifts in vinyloxy sulfides

In vinyloxy sulfides, **1**, **4** and **7**, the vinyl carbons adjacent to sulfur are strongly *shielded* relative to the α-carbons of divinyl sulfide (**11**). The ^{13}C chemical shift for C-3 in sulfide **1** is δ 86.66, 43.2 ppm upfield from the α-carbons in **11**; in **4**, despite the combined deshielding contributions of the α- and β-methylene groups,[16] C-10 absorbs at δ 98.36, 31.5 ppm upfield from the analogous carbons in **11**. The absorption for C-3 in **7** is 36.4 ppm more shielded than the α-carbon in **11**.

The vinylic carbons α to the ring oxygen in **1**, **4** and **7** are deshielded (24.5 to 32.5 ppm) relative to C-β in **11**. In **1**, the vinyl methyl group contributes to the

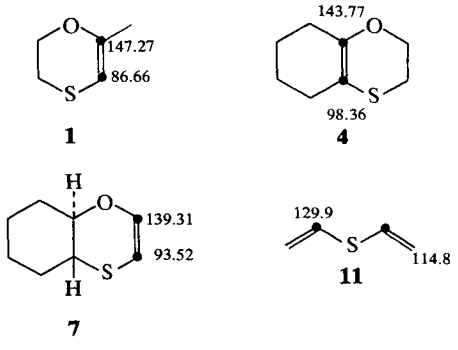
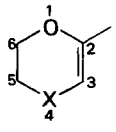
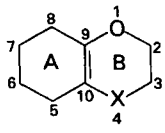


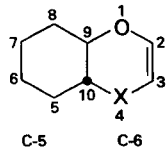
Table 1. ^{13}C NMR Chemical shifts of α,β-unsaturated cyclic sulfides, sulfoxides and sulfones



X	Compound	C-2	C-3	C-5	C-6	CH_3
S	1	147.27	86.66	24.20	65.84	21.51
SO	2	160.49	98.96	42.98	56.93	21.61
SO_2	3	162.47	102.62	48.71	65.86	21.12



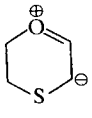
X	Compound	C-2	C-3	C-5	C-6	C-7	C-8	C-9	C-10
S	4	65.17	26.42	29.05	23.04	23.24	28.80	143.77	98.36
SO	5	56.23	44.60	25.96	22.13	22.70	28.65	155.50	109.24
SO_2	6	64.62	49.92	18.22	21.44	21.63	28.03	157.53	111.23



X	Compound	C-2	C-3	C-5	C-6	C-7	C-8	C-9	C-10
S	7	139.31	93.52	32.25	24.73	25.59	31.14	77.85	41.02
SO_{ax}	8	150.13	103.14	24.88	24.10	23.88	31.36	66.58	55.02
SO_{eq}	9	146.88	105.87	27.17	24.73	23.88	31.50	75.27	59.66
SO_2	10	150.08	105.52	18.20	22.42	22.64	30.26	77.92	60.33

deshielding of C-2 via the α-effect (~10 ppm)[16] while the influences of the C-5, C-7, and C-8 methylene groups in **4** combine to *shield* C-9 only slightly (~3.5 ppm) relative to C-2 in **1**. The resonance (*vide infra*) and inductive effects of the oxygen atom are primarily responsible for the deshielding of C-2 in **1** and **7** and C-9 in **4**. Miyzjima *et al.*[17] have indicated by calculation that in vinyl substituted compounds, the ^{13}C chemical shift of the α-carbon depends on the σ-electron density and is dominated by the inductive effect of the substituent.

In general, the magnitudes and signs of the shielding effects at C-2 (C-9) and C-3 (C-10) are suggestive of variations in the π electron density and/or carbon–carbon π bond order. The trends appear to be consonant with contributions from dipolar resonance structures I and II, where in principle, C-2 (C-9) possesses fractional positive charge and carbonyl character of 'reversed' polarity and C-3 (C-10) displays both partial negative charge and character of a thiocarbonyl carbon.



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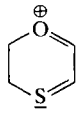
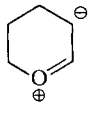
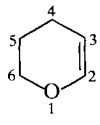


II

Several literature reports[18,19] indicate that both dipolar structures may be important in defining the electronic character of vinyl ethers and vinyloxy thioethers. For example, contributions from dipolar structure III adequately rationalize ^{13}C NMR shift differences at the vinylic carbons between cyclohexene (C-1 = C-2 = δ 127.33) and 2,3-dihydro-4*H*-pyran (**14**) [C-2 = δ 144.26 and C-3 = δ 100.54]. (The ^{13}C NMR data for cyclohexene and **14** were taken from Ref. 20. We note that while the structure and ^{13}C chemical shift assignments for **14** are correct, the name of the compound as reported in Ref. 20 is incorrect.) Parham *et al.*[19] compared the UV absorption data of **14**, 2,3-dihydro-4*H*-thiopyran (**15**), and 5,6-dihydro-1,4-oxathiin (**16**) and concluded that the long wavelength transition [λ_{max} 229 nm (ε 3820)] observed only in the case of **16** can best be interpreted in terms of contributions from structure II. (Apparently, **14** and **15**



III



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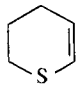

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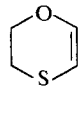

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exhibited no UV absorption maxima above 227 nm and absorptions below 226 nm could not be easily discerned due to instrumental restrictions.[19]) However, the anticipated chemical shifts arising from contributions of a thiocarbonyl carbon do not fully support the case for dipolar structure II. Thiocarbonyl carbons invariably appear downfield of olefinic as well as carbonyl carbons; consequently, a larger deshielding effect would be expected if contributions from II were significant. [Kalinowski and Kessler[21a,21b] have established a useful correlation between the ^{13}C NMR shifts of $^{13}C{=}O$ (amides) and $^{13}C{=}S$ (thioamides): $\delta_{C=S} = 1.45\,\delta_{C=O} - 46.5$ ppm. More recently, Pedersen *et al.*[21c] demonstrated that the ^{13}C chemical shifts of ketones and thioketones are similarly related: $\delta_{C=S} = 1.57\,\delta_{C=O} - 71.45$ ppm.]

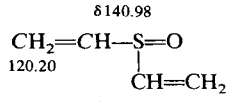
In this context, important consideration should be given to the results of nonempirical MO calculations of Bernardi *et al.*[22] and the *ab initio* SCF-MO calculations of Streitwieser and co-workers.[23] Both groups conclude that the principal mechanism for stabilization of *carbanions* adjacent to sulfenyl sulfur occurs through "polarization' rather than $(2p—3d)\pi$ conjugation. In this light, we suggest that dipolar structure I may actually achieve additional stabilization from the 'polarization' phenomenon, and may make a more significant contribution to the electronic description of **16** than II.

It is interesting that the π electron donor ability of oxygen in these vinyloxy ethers is in contrast to the expectations of sulfenyl sulfur in the light of the suggestion that π donating properties of various heteroatoms towards an adjacent carbocation center follow the series, P > S > N > O > Cl > F.[24]

SUBSTITUENT-INDUCED CHEMICAL SHIFT (SCS) EFFECTS IN SULFOXIDES AND SULFONES

In a previous report,[13] the substituent induced shifts on β-carbons resulting from oxidation of $-\overset{|}{S}-\rightarrow -\overset{|}{\underset{|}{S}}{=}O$ and $-\overset{|}{\underset{\|}{S}}{=}O$ (O) have been termed βSO and βSO_2 effects, respectively. The SCS effects referred to in this manuscript as βSO, βSO_2, γSO, and γSO_2 effects or values are determined from the differences in carbon shifts between the sulfinyl (sulfonyl) derivative and the parent sulfide [e.g., $\beta SO = \delta_C(S{=}O) - \delta_C(S)$]. Positive numbers reflect downfield shifts of that carbon upon oxidation of the sulfide to the sulfoxide or sulfone. In general, these effects are thought to arise from the inductive effect of the electropositive sulfinyl/sulfonyl sulfur and the substituent effect of the β-oxygen(s).[18a] The C-3 or C-10 vinylic carbons in sulfoxides **2**, **5**, **8**, and **9** are deshielded and exhibit βSO values ranging from 9.62 to 12.35 ppm. Similarly, C-3 and C-10 in sulfones **3**, **6** and **10** are also deshielded (e.g. βSO_2 values range from 12 to 16 ppm; Table 2) when compared to the analogous carbons in the vinyloxy sulfides **1**, **4** and **7**. It is noteworthy that the magnitude of the βSO and βSO_2 effects at the vinyl carbons are 4.4–10.6 ppm less than the SCS effects observed at the saturated β carbons (e.g. βSO and βSO_2 values at sp^3 carbons average ~20 ppm).

Interestingly, the βSO effect (11.03 ppm) in divinyl sulfoxide (**17**) is similar to the βSO effects found for the vinylic carbons in sulfoxides **2**, **5**, **8** and **9**. By contrast, the βSO_2 effect (7.24 ppm) for divinyl sulfone (**18**) is diminished considerably when compared with the βSO_2 effects at the vinylic carbons for sulfones **3**, **6** and **10**.



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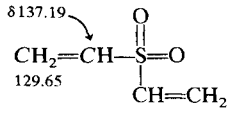

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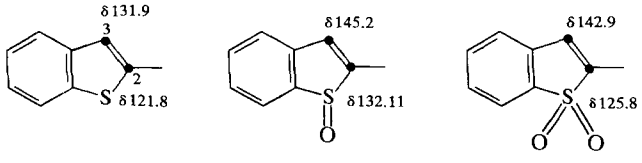
Table 2. Substituent-induced chemical shift effects (βSO, βSO_2, γSO and γSO_2 effects)[a]

Compound	βSO C-3	βSO C-5	βSO C-10	βSO_2 C-3	βSO_2 C-5	βSO_2 C-10	γSO C-2	γSO C-5	γSO C-6	γSO C-9	γSO_2 C-2	γSO_2 C-5	γSO_2 C-6	γSO_2 C-9
2	12.30	18.78					13.22		−8.91					
3				15.96	24.51						15.20		0.02	
5	18.18		10.88				−8.94	−3.09		11.73				
6				23.50		12.87					−0.55	−10.83		13.76
8	9.62		14.00				10.72	−7.37		−11.27				
9	12.35		18.64				7.57	−3.97		−2.58				
10				12.00		19.31					10.75	−14.01		0.07

[a] The substituent effects (i.e. βSO, βSO_2, etc.) are calculated as $\Delta\delta = \delta_C S(O)_n - \delta_C(S)$ where $n = 1,2$ (see text).

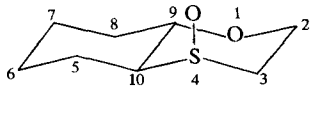
The absence of large βSO and βSO_2 values at sp^2 carbons may be due to several or a combination of different factors including (1) a reduction in a sizeable oxygen atom substituent effect at sp^2 carbon compared to the adjacent sp^3 carbon; (2) differences in the inductive effects of SO and SO_2 groups through $3sp^3$—$2sp^3$ and $3sp^3$—$2sp^2$ bonds;[25] (3) electropositive sulfur induced polarization of π density towards C-β;[26] (4) $(2p—2p)\pi$ bond resonance interactions between the vinyl carbons and the ring oxygen;[18] (5) electric field induced polarization of C—C π density towards C-β;[27] and (6) π conjugative interactions between the ring oxygen and the sulfinyl or sulfonyl sulfur. Although a clear experimental distinction between any of these factors cannot presently be ascertained with a high level of certainty, it is clear that the diminished βSO and βSO_2 effects at sp^2 carbons are independent of a $2p\pi$ donor heteroatom (e.g. oxygen). The ^{13}C NMR shifts for a series of benzo[*b*]thiophens and the *S*-oxides have been reported, and the basic trends in shifts as a function of oxidation in the five-membered ring are similar to those observed here: βSO = 10.30, βSO_2 = 4.0, γSO = 13.3, and γSO_2 = 11.0 ppm.[28]) In the light of the relatively small βSO



and βSO_2 effects in divinyl sulfoxide and divinyl sulfone, explanations based on changes in π electron density or bond order caused by polarization or resonance interactions appear attractive. (The βSO and βSO_2 effects for divinyl sulfoxide and divinyl sulfone, respectively, are smaller than those determined for their saturated analogs [diethyl sulfoxide (βSO = 19.33); diethyl sulfone (βSO_2 = 20.62 ppm)].[29])

The γ vinylic carbons in both the sulfoxides and sulfones are *deshielded*; γSO values range from 7.6 to 13.2 ppm in the former and γSO_2 values vary from 10.7 to 15.2 ppm in the latter. These effects are generally in sharp contrast to γSO and γSO_2 effects at sp^3 γ carbons which, with only two exceptions where essentially no shift occurs (e.g. C-6 in **3** and C-9 in **10**), are shielded. The fact that γSO_2 values at selected sp^3 carbons (e.g. C-6 in **3**; C-2 in **6**; C-9 in **10**) are essentially zero (<1 ppm) implies that the shielding effect normally associated with the γ *gauche* array between sulfonyl oxygen and carbon in chair conformations of 6-membered rings[13] is negated in the 1,4-oxathiin *S,S*-dioxides. The differences in predicted and observed shifts in the sulfones are probably related to the differences in spatial proximity of the interacting groups in *trans*-1,4-oxathiadecalin 4,4-dioxide and the various 1,4-oxathiin 4,4-dioxides reported here. This contrast is most apparent in the γSO values in sulfoxide **5**. At C-9, the positive γSO value (11.73 ppm) indicates deshielding at the sp^2 carbon relative to C-9 in sulfide **4**; at C-2 the expected shielding γSO effect (−8.94 ppm) is observed, while a smaller shielding γSO effect (−3.09 ppm) is found at C-5 which is 'pseudo-*gauche*' to both the sulfinyl lone pair electrons and the sulfinyl oxygen. Examination of Dreiding molecular models of **4** and **5** reveals the potential for conformational flexibility in the heterocyclic ring. In fact, the B ring of **4** and **5** may actually exist in slightly flattened boat conformations; therefore, sulfoxide **5** may be a dynamic equilibrium of 'axial' and 'equatorial' sulfinyl conformers and its ^{13}C shifts would be the weighted average of conformers.

The axial-equatorial stereochemical assignment of the sulfinyl group in **8** and **9** was based on comparisons of the magnitudes of the βSO and γSO effects at C-9 and C-10 of the isomeric *trans*-1,4-oxathiadecalin 4-oxides (**19** and **20**). In these systems, the βSO values are 12.7 (axial SO; **19**) and 21.2 ppm (equatorial S=O; **20**) while the γSO values are −12.45 (axial S=O) and −5.29 ppm (equatorial S=O).



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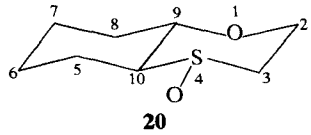

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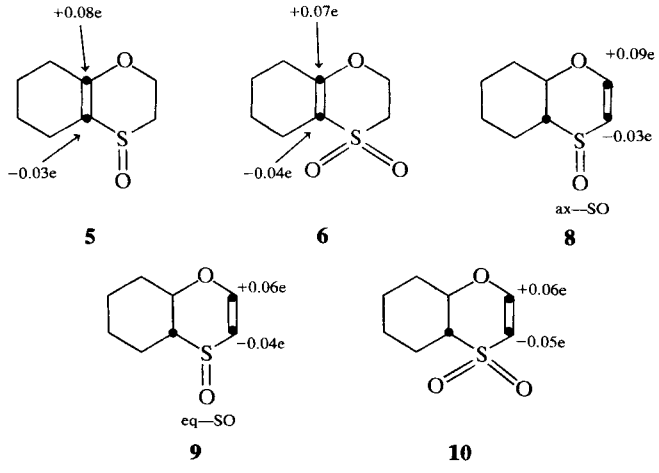
It seems reasonable to assume that of the two isomeric sulfoxides **8** and **9**, the isomer of the pair with the smaller βSO value and larger γSO value should be the axial sulfoxide **8**, in keeping with the previously established trends.[13] It is, however, quite clear that the γSO effects at C-2 in **8** and **9** are large and *deshielding*.

Rough estimates of the extent of π electron distribution at the vinylic carbons, C-β and C-γ, in both the vinyloxy sulfoxides and sulfones can be made using the empirical procedure of Loots *et al.*[30] (The procedure of Loots *et al.*[30] seems to overestimate π electron densities when comparisons are made with available calculated densities by other methods; however, the observed trend between CNDO results and those calculated by the procedure of Loots *et al.* suggest a

rough correlation.) The assumptions inherent in this empirical procedure do not allow for a quantitative evaluation of the dispersal of π electron densities, but the trends clearly indicate that, on average, nearly twice as much π electron density is lost at C-γ (+0.07 π electron) than gained at C-β (−0.04 π electron) of the vinyl group. [The procedure used here involved the use of the equation

$$Z_\pi = Z_{tot} - Z_\sigma$$

where Z_π, Z_{tot} and Z_σ represent the changes in π, total and σ electron density at a given carbon. Estimates of Z_{tot} may be calculated by obtaining the difference in the C-β (or C-γ) chemical shifts of the unsaturated sulfoxide (sulfone) and the unsaturated sulfide. Z_σ is simply the difference in chemical shift between C-β (or C-γ) in the saturated sulfoxide (sulfone) and C-β (C-γ) in the sulfide. A positive value for Z_π, divided by 240 ppm per electron,[31] corresponds to a loss in π electron density while a negative value reflects a gain in π electron density.]



5 6 8

9 10

EXPERIMENTAL

Melting points were obtained in a Mel-Temp melting point apparatus with an open capillary tube and are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc. and Integral Microanalytical Laboratories, Inc.

^{1}H NMR spectra were recorded on Varian Model XL-100-12 (100.06 MHz, 23 487G) and Perkin-Elmer Model R24B (60 MHz, 14 092G) NMR spectrometers. Additional spectra were recorded on the Bruker Model WP-200 NMR spectrometer at the South Carolina Nuclear Magnetic Resonance Laboratory under NSF Grant No. CHE 78-05921. The ^{13}C NMR FT spectra were recorded on a Varian Model XL-100-12 NMR spectrometer controlled by a 620/f computer at 25.16 MHz with a pulse width of 7 μs. All ^{13}C and ^{1}H NMR FT spectra were obtained at a probe temperature of 25° and Fourier transforms were based on 8K data points with off-resonance and noise decoupling. All ^{1}H and ^{13}C NMR chemical shifts of samples as 5–15% (w/w) deuteriochloroform ($CDCl_3$), deuterated dimethyl sulfoxide [$CD_3S(O)CD_3$], or deuterium oxide (D_2O) solutions are presented in parts per million (δ) downfield from internal tetramethylsilane (Me_4Si). Dioxane (δ 67.8) was also used as internal standard. The digital resolution for FT determinations is 0.625 Hz.

General procedure for oxidation of sulfides to sulfoxides and sulfones with *m*CPBA

A solution of *m*CPBA (1 equivalent for sulfoxides and 2 equivalents for sulfones) in dichloromethane (CH_2Cl_2) was added dropwise (1 h) to a solution of the sulfide (1 equivalent) in CH_2Cl_2 [0–5° (ice bath) for sulfoxides and 25° for the sulfones]. The solution was stirred at 0–5° for 6–8 h (for sulfoxides) or overnight at 25° (for the sulfones), then washed with a saturated solution of sodium bicarbonate (100 ml) and water (100 ml) and finally dried over magnesium sulfate. Removal of the solvent (rotary evaporator) gave the sulfoxide or sulfone, generally as a solid. Purification by recrystallization and/or column chromatography afforded homogeneous material.

5,6-Dihydro-2-methyl-1,4-oxathiin (1). 2,3-Dichloropropene (18.5 g, 0.17 mol) was added over a period of 1 h to an ethanolic solution (50 ml) of sodium hydroxide (6.7 g, 0.17 mol) and 2-mercaptoethanol (13 g, 0.17 mol). After the addition was completed, stirring was discontinued and the solution was allowed to stand overnight.

The solution was then refluxed for 1 h, allowed to cool to ambient temperature, and washed with water (3×30 ml). The washings were extracted with dichloromethane (2×50 ml). The original organic layer and the organic washings were combined, dried, filtered, and reduced to a yellow liquid. Distillation afforded 17.7 g (69%) of 2-(2-chloroallylthiol-ethanol): b.p. 98–110°/2.3 torr [lit.,[8a] 92–95°/3 torr].

The chloroallyl compound (15.2 g, 0.10 mol) was refluxed in an aqueous solution (100 ml) of sodium hydroxide (8 g, 0.2 mol) for 3 h. After it had cooled, the solution was extracted with dichloromethane (3× 50 ml). The organic layer was dried, filtered, and reduced to a yellow liquid. Distillation yielded 1.52 g (13.1%) of **1**: b.p. 47–51°/4.6 torr [lit.,[8a] 74–75°/35 torr].

5,6-Dihydro-2-methyl-1,4-oxathiin 4-oxide (2). Oxathiin **1** was oxidized according to the general procedure to afford sulfoxide **2**. The crude material was purified by column chromatography (Al_2O_3, CH_2Cl_2, then CH_2Cl_2:EtOAc 1:1 as eluants) to give a colorless solid: m.p. 86.5–88.0°. Anal. calcd: C, 45.43; H, 6.11; S, 24.25. Found: C, 45.18; H, 6.17; S, 23.63.

5,6-Dihydro-2-methyl-1,4-oxathiin 4,4-dioxide (3). Oxidation of **1** by the general procedure gave sulfone **3**. The crude material was purified by column chromatography (Al_2O_3, C_6H_{12}:CH_2Cl_2, then CH_2Cl_2 as eluants) to give a colorless solid: m.p. 71.5–74.5°. Anal. calcd: C, 40.52; H, 5.45; S, 21.63. Found: C, 40.61; H, 5.33; S, 21.30.

1,4-Tetrahydro[9,10]benzoxathiin (4). Cyclohexanone (9.8 g, 0.10 mol), 2-mercaptoethanol (7.8 g, 0.10 mol),

and a catalytic amount of *p*-TsOH (0.4 g) were subjected to azeotropic distillation in benzene for 6 h.[8]

After the solution had cooled and a solid precipitate had been removed by filtration, the benzene solution was washed with 5% aqueous $NaHCO_3$ (2×50 ml), dried, and filtered. Removal of the benzene yielded an opaque liquid which, upon distillation, afforded 6.8 g (43%) of the oxathiolane: b.p. 68.5°/3.1 torr.

To a dichloromethane solution of the oxathiolane (4.7 g, 0.030 mol) was added *m*CPBA (6.0 g, 0.030 mol) in dichloromethane. The resulting solution was allowed to reach ambient temperature overnight. The solution was washed with 5% aqueous $NaHCO_3$ (3×50 ml), dried and filtered. Removal of the solvent gave 4.7 g (92%) of an opaque liquid.

The sulfoxide was azeotropically distilled in benzene (100 ml) for 20 h in the presence of a catalytic amount of *p*-toluenesulfonic acid (0.5 g). After it had cooled the solution was washed with 5% aqueous $NaHCO_3$, dried and filtered. Removal of solvent and distillation afforded 1.24 g (29.4%) of a clear, colorless liquid: b.p. 58–61°/0.28 torr [lit.,[2a] 73–74°(1.4 torr)].

1,4-Tetrahydro[9,10]benzoxathiin 4-oxide (5). Sulfoxide **5** was obtained by oxidation with *m*CPBA using the general procedure. A homogeneous sample of the material was obtained by column chromatography (Al_2O_3, CH_2Cl_2, then CH_2Cl_2:EtOAc 1:1): m.p. 83–85° [lit.,[2a] 86–87°]. Anal. calcd: C, 55.79; H, 7.02; S, 18.61. Found: C, 55.36; H, 6.72; S, 18.50.

1,4-Tetrahydro[9,10]benzoxathiin 4,4-dioxide (6). Oxidation of **4** with excess *m*CPBA following the general procedure gave sulfone **6**. A homogeneous sample of the compound was obtained by column chromatography (Al_2O_3, CH_2Cl_2): m.p. 117.4–119.5° [lit.,[2a] m.p. 115–116°]. Anal. calcd: C, 51.04; H, 6.44; S, 17.03. Found: C, 50.78; H, 6.68; S, 16.76.

***trans*-Tetrahydro-1,4-benzoxathiin 4-oxides (8, 9).** A mixture of the compounds was obtained by oxidation of sulfide **7**[2a,9b] with one equivalent of *m*CPBA, followed by column chromatography (Al_2O_3, CH_2Cl_2 then CH_2Cl_2:EtOAc 1:1). Anal. calcd: C, 55.79; H, 7.02; S, 18.61. Found: C, 55.81; H, 7.33; S, 18.04.

Divinyl sulfide (11). A 200-ml pear-shaped flask with a 12 inch vacuum jacketed Vigreux column was evacuated and filled with dry nitrogen gas. 2,2'-Thiodiethanol (12.2 g, 10.0 ml, 100.0 mmol) and potassium hydroxide (10.0 g, 210 mmol) were placed in the flask and heated in an oil bath at 200° and the liquid distillate was collected in a dry ice cooled receiver (boiling range 53–92° at 750 torr). The lower water layer of the distillate was discarded and the upper organic phase was dried (sodium carbonate) and distilled under an inert atmosphere (nitrogen gas) to afford 1.6 g (19%) of a colorless liquid: b.p. 68–72° (750 torr) [lit.,[11] b.p. 42.5°(150 torr)]. The product was stored under a nitrogen atmosphere in a freezer to retard polymerization.

Divinyl sulfoxide (12). Divinyl sulfide was oxidized with one equivalent of *m*CPBA in dichloromethane at a very slow rate according to the general procedure and a nitrogen atmosphere was necessary to minimize polymerization (64% yield): b.p. 21–23° (0.025 torr) [lit.,[12] b.p. 58–59°(3.5 torr)].

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