Carbon-13 Nuclear Magnetic Resonance Spectra of Thioalkylacetaldehyde Dimethyl Acetals, *S*-Oxides, and *S*,*S*-Dioxides

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Carbon-13 NMR chemical shifts of alkylthioacetaldehyde dimethyl acetals, *S*-oxides, and *S*,*S*-dioxides are reported. The deshielding β_{SO} and β'_{SO} effects are large and range from 13.05 to 23.14 ppm. The β_{SO} effect is sensitive to structural variations while β'_{SO} is essentially invariant. The deshielding β_{SO_2} and β'_{SO_2} effects parallel the β_{SO} and β'_{SO} effects and show only a small change due to the additional oxygen atom on sulfur. The γ and γ' effects in the sulfinyl and sulfonyl derivatives are shielding relative to the sulfides with values averaging −8.3 ppm for γ_{SO} and γ_{SO_2} and about −5 ppm for γ'_{SO} and γ'_{SO_2}. The relationships between ^{13}C NMR shifts and structure are discussed.

From the numerous accounts describing factors likely to influence NMR chemical shifts significantly, it is clear that ^{13}C NMR shifts are a function of many parameters which are related in a complex manner.[1-3] At the present time, it appears that the possibility of establishing a general theory for predicting the influence of substituents on ^{13}C shifts is somewhat remote.[4] However, an alternative and quite useful approach is to consider effects of a group of substituents which are closely related and monitor the variations in ^{13}C shifts with the change in the intrinsic properties of the substituents. The results obtained from such comparisons could be used to establish useful correlative data for application in other systems with similar substituents.

There currently exists little systematic ^{13}C NMR data on organosulfur compounds, particularly divalent sulfur, and the corresponding *S*-oxide and *S*,*S*-dioxide derivatives. Here we describe the syntheses of a series of alkylthioacetaldehyde dimethyl acetals, the sulfoxides, and the sulfones and a number of useful trends in their ^{13}C NMR shifts. These compounds were found to be useful probes while attempting to understand and describe the nature of attractive intramolecular interactions between ether oxygens and alkylsulfinyl groups in simple acyclic molecules.[6] Attractive intramolecular interactions between oxygen and "electropositive" sulfinyl (and sulfonyl) sulfur have been previously postulated in anancomeric 1,3-dioxanes.[7]

Results and Discussion

Syntheses. Typically, the corresponding alkylthioacetaldehyde dimethyl acetals were prepared by reacting an ethanolic solution of the appropriate potassium alkylthiolate ($K^+{}^-SR$) with chloroacetaldehyde dimethyl acetal. The sulfoxides were prepared by oxidation of the sulfides with sodium metaperiodate ($NaIO_4$)[8] and because of the acid lability of the dimethyl acetal functional group, the sulfones were synthesized by neutral potassium permanganate ($KMnO_4$) oxidation[9] of the corresponding sulfoxides. The preparative routes to the compounds described herein are shown in Scheme I.

Scheme I

$$ClCH_2CH(OCH_3)_2 + K^+{}^-SR \xrightarrow[2.\ \text{heat, 4 h, reflux}]{1.\ KOH,\ EtOH,\ 0\text{–}5\ ^\circ C}$$

$$RSCH_2CH(OCH_3)_2 \quad \mathbf{1, 4, 7, 10} \xrightarrow[2.\ 25\ ^\circ C,\ 18\ h]{1.\ NaIO_4,\ CH_3OH\text{–}H_2O,\ 0\text{–}5\ ^\circ C}$$

$$RS(O)CH_2CH(OCH_3)_2 \quad \mathbf{2, 5, 8, 11} \xrightarrow{KMnO_4,\ H_2O,\ 25\ ^\circ C}$$

$$RS(O_2)CH_2CH(OCH_3)_2 \quad \mathbf{3, 6, 9, 12}$$

R = Me, Et, *i*-Pr, *t*-Bu

NMR Spectral Data. The ^{13}C NMR shift assignments were based on anticipated shifts due to the inductive/field effects[10] of oxygen and sulfur, particularly for the sulfoxides and sulfones,[10c] in conjunction with the multiplicity of the carbon signals during coherent proton off-resonance decoupling experiments.[11] The data are discussed in terms of β, β', γ, and γ' effects as substitution on both carbon and sulfur is altered. Thus, the β and β' carbons are adjacent to the sulfur atom and β to the substituent on the sulfur atom (e.g., lone pair electrons or oxygen atom). The β' carbon has the same structural relationship to the substituents on sulfur as the β carbon except that it is bonded to the acetal carbon.[12]

$$C_\gamma—C_\beta—X—C_{\beta'}—C_{\gamma'}(OCH_3)_2$$
$$X = S, SO, SO_2$$

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(11) R. R. Ernst, *J. Chem. Phys.*, **45**, 3845 (1966).
(12) Although the α effect is not explicitly mentioned here, the data in Table I pertaining to the ^{13}C NMR chemical shifts of C_β (C_5) for the sulfide series are consistent with previous reports for increased methyl substitution in hydrocarbons.[13,14]
(13) (a) P. C. Lauterbur, *Ann. N.Y. Acad. Sci.*, **70**, 841 (1958); (b) L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971); (c) H. Duddeck and P. Wolff, *Org. Magn. Reson.*, **8**, 593 (1976).

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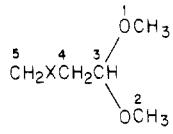
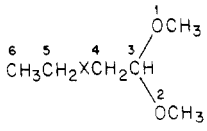
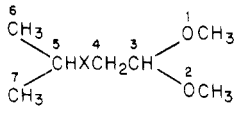
Table I. ^{13}C NMR Shifts of Alkylthioacetaldehyde Dimethyl Acetals, *S*-Oxides, and *S,S*-Dioxides



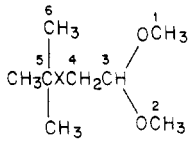
1 (X = S)	$C_5 = 16.29$, $C_4 = 36.42$, $C_3 = 104.71$, $C_1 = C_2 = 53.38$
2 (X = $SO)_2$	$C_5 = 39.43$, $C_4 = 57.66$, $C_3 = 99.29$, $C_1 = 54.58$, $C_2 = 53.49$
3 (X = SO_2)	$C_5 = 42.22$, $C_4 = 57.23$, $C_3 = 99.75$, $C_1 = C_2 = 53.46$



4 (X = S)	$C_6 = 14.76$, $C_5 = 26.66$, $C_4 = 34.00$, $C_3 = 104.73$, $C_1 = C_2 = 53.46$
5 (X = SO)	$C_6 = 6.59_8$, $C_5 = 46.29$, $C_4 = 54.94$, $C_3 = 99.51$, $C_1 = 54.64$, $C_2 = 53.52$
6 (X = SO_2)	$C_6 = 6.41$, $C_5 = 48.48$, $C_4 = 54.82$, $C_3 = 99.91$, $C_1 = C_2 = 54.22$



7 (X = S)	$C_6 = C_7 = 23.39$, $C_5 = 35.32$, $C_4 = 32.971$, $C_3 = 104.61$, $C_1 = C_2 = 53.44$
8 (X = SO)	$C_6 = 13.73$, $C_7 = 15.26$, $C_5 = 49.96$, $C_4 = 51.63$, $C_3 = 99.30$, $C_1 = 54.13$, $C_2 = 53.02$
9 (X = SO_2)	$C_6 = C_7 = 14.97$, $C_5 = 52.66$, $C_4 = 53.49$, $C_3 = 99.93$, $C_1 = C_2 = 54.22$



10 (X =S)	$C_6 = 30.82$, $C_5 = 41.84$, $C_4 = 30.97$, $C_3 = 103.86$, $C_1 = C_2 = 53.13$
11 (X = SO)	$C_6 = 24.67$, $C_5 = 54.89$, $C_4 = 51.43$, $C_3 = 102.64$, $C_1 = 56.92$, $C_2 = 55.75$
12 (X = SO_2)	$C_6 = 23.12$, $C_5 = 59.86$, $C_4 = 49.82$, $C_3 = 99.04$, $C_1 = C_2 = 53.86$

Table II. The β_{SO}, β'_{SO}, β_{SO_2}, and β'_{SO_2} Effects in Alkylthioacetaldehyde Dimethyl Acetal Sulfoxides and Sulfones

$R-C_\beta-X-C_{\beta'}-C(OMe)_2$
X = S, SO, SO_2

substituent, R	β_{SO}	β'_{SO}	β_{SO_2}	β'_{SO_2}
H (Me)	23.14	21.24	25.93	20.81
CH_3 (Et)	19.63	20.94	21.82	20.82
$(CH_3)_2$ (*i*-Pr)	14.64	18.66	17.34	20.52
$(CH_3)_3$ (*t*-Bu)	13.05	20.46	18.02	18.85

[a] β_{SO}, β'_{SO}, β_{SO_2}, and β'_{SO_2} shifts are determined from the differences in carbon shifts between the sulfinyl and sulfonyl derivative and the parent sulfide (e.g., $\beta_{SO} = \delta_{SO} - \delta_S$). Positive numbers reflect downfield shifts of that carbon upon oxidation of the sulfide to the sulfoxide or sulfone.

β Effects. Oxidation of the alkylthio group (RS–) to the sulfinyl derivative (RS(O)–) in the alkylthioacetaldehyde dimethyl acetals results in the expected downfield shifts of the attached carbons β ($\Delta\delta$ ranges from 14.64 to 23.14 ppm) and β' ($\Delta\delta$ ranges from 18.66 to 21.24 ppm) to the sulfinyl oxygen atom (Table II). This "β_{SO} effect", where $\Delta\delta = \delta_{C_\beta}$(sulfoxide) – δ_{C_β}(sulfide), is thought to arise from the low-field shift of a β effect caused by the oxygen substituent on sulfur coupled with an inductive effect resulting from the partial positive charge on the sulfinyl sulfur.[15,16] The inductive effect or electronegative influence of divalent sulfur and its various oxidized forms on adjacent carbon shifts deserves comment. Lambert[16] has recently demonstrated that increased electronegativity results from the introduction of a positive and, presumably a partial positive, charge on a heteroatom and the observed shift difference is linearly related to the change in electronegativity (45 ppm/electronegativity unit.)[17]

The data in Table II show that the β_{SO} and β'_{SO} effects are quite similar for methyl and ethyl derivatives, but with further substitution the β_{SO} effect diminishes considerably from the average value of β'_{SO} (20.32 ppm). This decrease in β_{SO} reflects *less deshielding* at C_β. It has been argued that in some cases the decreasing β substituent effects in hydrocarbons can be adequately interpreted in terms of increased synclinal interactions.[18] However, in light of earlier proposals by Stothers[19] and more recently Gorenstein[20] where the suggestion is made that carbon as well as phosphorus and fluorine chemical shifts are influenced by bond and torsional angle interactions, it would seem useful to consider the data from this perspective. The prediction is made that bond angle widening caused by severe steric perturbations within a molecular fragment (particularly for conformations involving synclinal interactions) will result in *increased shielding* of the atoms involved.[19,20] It does seem apparent from the data in Table II that the magnitude of β_{SO} decreases substantially with increased methyl substitution and appears to parallel the rise in steric congestion.[21]

With the increase in synclinal interactions about the C_β–S single bond with methyl substitution at C_β, an increase in the shielding of $C_{\beta'}$ might also be expected. With exclusion of R = *i*-Pr, the trend in β'_{SO} is in the anticipated shielding direction, although the overall magnitude is low. This small change in β'_{SO} is, of course, understandable since $C_{\beta'}$ experiences essentially the same synclinal interaction of the R group in both the sulfide and sulfoxide.

Further oxidation of the sulfinyl group to the sulfonyl group *does not* substantially deshield either C_β or $C_{\beta'}$ (Table II).[22] The absence of any noticeable inductive effect of the sulfonyl group over the sulfinyl group suggests that the increased inductive character of the sulfonyl group[25] toward C_β and $C_{\beta'}$ has been effectively *neutralized*. Although presently unexplained, this phenomenon is in agreement with other observations where geminal substitution (C_β–CHX → C_β–CX_2) hardly affects C_β chemical shifts.[26] For example, C_2,C_6 carbons in cyclohexanone

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(22) This is in contrast to the relatively large hydrogen chemical shift differences ($\Delta\delta$ ranges from 0.35 to 0.50 ppm) for aliphatic[23] and aryl methyl[24] sulfoxides and sulfones.
(23) G. Barbarella, P. Dembeck, A. Garbesi, and A. Fava, *Org. Magn. Reson.*, **8**, 108 (1976).
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dimethyl ketal (δ 32.9) have essentially the same resonance as C_2,C_6 in methoxycyclohexane (δ 32.3).[26]

γ Effects. Some interesting observations were made when the effects of the sulfinyl and sulfonyl groups on C_γ and $C_{\gamma'}$ chemical shifts were examined (see Table I). From previous studies,[27] we expected the sulfinyl group to shield C_γ and we observed a −8.17 ppm shift from **4** → **5**. The average value of −8.90 ppm for the diastereotopic isopropyl methyl in **7** → **8** is observed for γ_{SO} and the *tert*-butyl methyls in **11** are shielded by −6.15 ppm when compared to the appropriate sulfide, **10**. A number of explanations have been presented to account for the shieldings of carbons having a synclinal and antiperiplanar γ relationship with sulfinyl oxygens. In some cases, explanations analogous to the original proposal of Cheney and Grant[28] regarding the γ gauche steric shift effect and possible conjugative transfer of charge (γ anti effect) as recently proposed by Eliel et al.[29] have been useful. An alternate explanation involving linear electric field induced shifts where a carbon atom experiences upfield shifts when a C–H bond is proximal to the negative end of an electric dipole deserves careful consideration.[30]

The γ_{SO} effects reported here [(−6.15 to −8.90 ppm)] are larger than those reported between γ gauche carbons in cyclic and acyclic hydrocarbons,[28,31] but smaller than other values reported for C_γ carbons in conformationally homogeneous sulfoxides.[32]

The γ_{SO} effect in **11** is diminished by approximately 2 ppm over γ_{SO} for **5**. We rationalize this difference as being due to rotational averaging of the *tert*-butyl methyls and possibly *deshielding* by the sulfinyl oxygen atom. Concerning this result, Stothers has shown that the antiperiplanar γ effects from a variety of substituents are deshielding if the effect is transmitted through quaternary carbons.[33]

By contrast, the γ'_{SO} effect is essentially constant: γ'_{SO} is −5.42 for **2**, −5.22 for **5**, and −5.31 ppm for **8**. This constancy is expected provided the conformational distribution about the CH_2–CH single bond of the three sulfoxides is essentially unchanged. This suggestion is supported by the similarity in the vicinal hydrogen–hydrogen coupling constants: $J_{AC} = J_{BC} = 5.78$ Hz for **2**, $J_{AC} = J_{BC} = 5.81$ Hz for **5**, and $J_{AC} = 6.22$ and $J_{BC} = 5.55$ Hz for **8** in deuteriochloroform solvent at 25 °C.

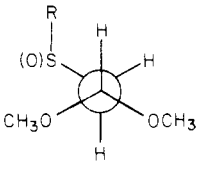
$$RS(O)CH_AH_BCH_C(OCH_3)_2$$

The γ'_{SO} value for **11** (−1.12 ppm) is smaller than anticipated. Examination of the vicinal hydrogen–hydrogen coupling constants for **11** (^3J = 7.07 and ^3J = 4.75 Hz) suggest that rotamer I may be more than statistically populated. If so, it seems reasonable to suggest that the probability of a deshielding contribution from the δ effect would likewise increase.

Table III. Anisochronism (Δδ) of Geminal Probes in $RS(O)CH_2CH(OCH_3)_2$[a,b]

compd	R	Δδ-[-SO-CH_2-]	Δδ-[-CH(O-CH_3)$_2$]	Δδ[-CH(O^{13}-CH_3)$_2$]
2	CH_3	0.00	2.66	27.6 (1.09)[c]
5	CH_2CH_3	0.00	3.23	28.1 (1.12)
8	$CH(CH_3)_2$	0.29	3.86	27.9 (1.11)
11	$C(CH_3)_3$	1.62	4.32	29.3 (1.17)

[a] ^{1}H and ^{13}C NMR data were obtained on the sulfinyl derivative as dilute (see Experimental Section) deuteriochloroform solutions at ambient temperature and at 60 and 25.2 MHz, respectively. [b] All data are reported in hertz (Hz). [c] In ppm.



I

In the sulfide–sulfone comparisons, the γ_{SO_2} and γ_{SO} effects are virtually identical: shielding of C_γ from **4** → **6** is −8.35; **7** → **9** is −8.42; **10** → **12** is −7.70 ppm. The presence of a sulfur atom in the chain appears to be unimportant as evidenced by the correlation of ^{13}C chemical shifts between alkyl sulfones and the corresponding hydrocarbons: $C_\gamma(SO_2) = [(1.020 \pm 0.025)C_\gamma\text{-(alkyl)} - (8.04 \pm 0.62)]$.[34] This implies that the electron pair(s) on divalent sulfur at least in acyclic systems have essentially the same influence on the ^{13}C chemical shift of C_γ as a methylene group. Qualitatively, it seems reasonable to expect the sulfonyl oxygens to interact with the proximal C_γ carbons in a manner similar to that characterized by the sulfinyl oxygen atom. However, since the overall effect is about the same, the inductive effect of the SO_2 group must be partially offset by the ability of the two oxygens to shield C_γ presumably via a γ gauche mechanism.

The acetal carbon, $C_{\gamma'}$, exhibits a similar pattern of shift differences for methyl through *tert*-butyl when comparing the sulfones with the sulfides with practically no variation in γ'_{SO_2} (average value = 4.82 ppm).

Diastereotopic Methyls. Geminal anisochronism at prochiral centers is a commonly observed phenomenon in NMR spectroscopy and various aspects of this subject have received considerable comment.[35,36] Since the sulfinyl sulfur is chiral, the geminal acetal methyl hydrogens and carbons for the sulfinyl derivatives **2**, **5**, **8**, and **11**, including the isopropyl methyls in **8**, should, in principle, exhibit anisochronism.[37]

The ^{13}C chemical shifts of the geminal methyls of the isopropyl group in sulfoxide **8** are δ 13.73 and 15.26 (Δδ = 1.63). This Δδ value is comparable to those of other diastereotopic methyls where the geminal probe is one bond removed from the chiral center.[38] The spread in Δδ values of the acetal methyls is small, ranging from 1.09 to 1.17 ppm, suggesting a low sensitivity to the change in alkyl substituent, R (see Table III). Generally, the shielding difference between diastereotopic methyl carbons is ex-

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(28) B. V. Cheney and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 5319 (1967).
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(30) (a) J. G. Batchelor, *J. Am. Chem. Soc.*, **97**, 3410 (1975); (b) J. G. Batchelor, J. H. Prestegard, R. J. Cushley, and S. R. Lipsky, *J. Am. Chem. Soc.*, **95**, 6358 (1973); (c) J. G. Batchelor, *J. Magn. Reson.*, **18**, 212 (1975).
(31) The γ gauche effect for the methyls in *n*-butane is −2.5 ppm.[28]
(32) See ref 27b.
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(35) W. B. Jennings, *Chem. Rev.*, **75**, 307 (1975).
(36) W. B. Jennings, S. Al-Shewiman, M. S. Tolley, and D. R. Boyd, *Org. Magn. Reson.*, **9**, 151 (1977).
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(38) A. Ejchart, *Org. Magn. Reson.*, **9**, 351 (1977).

pected to decrease monotonically with increasing separation of the probe(s) from the chiral center.[35,39,40] In the sulfoxides described here the distance between the sulfinyl group and the acetal carbons is constant, although the steric environment about the chiral sulfoxide increases. It has been previously shown that for systems in which diastereotopic methyls are bonded directly to a chiral center, *i*-PrCH(OH)R, $\Delta\delta$ increases, from 0.2 to 7.2 ppm, as R changes from methyl to *tert*-butyl.[41] Our data suggest that $\Delta\delta$ is appreciable yet *invariant* when the chiral center is four bonds removed from the geminal probes. The fact that the shift differences are nearly constant implies that the acetal methyls are largely confined to an environment which is insensitive to substitution or where changes in the rotamer population about the S–CH_2 bond do not affect significantly the diastereotopism of the acetal methyls. Surprisingly, the diastereotopic acetal methyls of **11** are shifted to lower field (δ 56.92 and 55.75) in comparison with the geminal methoxyls in **2**, **5**, and **8**. Although the reason for this is not immediately apparent, it does seem likely that a change in the rotamer population could be responsible (vide supra).

The data in Table III is a summary of the anisochronism exhibited for both methylene and methyl groups of the sulfinyl compounds. It is noteworthy that the anisochronism of the methylene hydrogens is small while the hydrogens five bonds removed from the chiral center show larger shift differences.[6]

Experimental Section

Melting points were obtained in a Melt-Temp melting point apparatus with an open capillary tube and are uncorrected.

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and Integral Microanalytical Laboratories, Inc., Raleigh, N.C.

^{1}H NMR spectra were recorded on JEOL Model C-60-HL and Varian Model XL-100-12 NMR spectrometers. ^{13}C NMR FT spectra were recorded on a Varian Model XL-100-12 NMR spectrometer controlled by a 620/f computer. All FT spectra were obtained at ambient temperature (~30 °C) and all Fourier transforms were based on 8K data points with off-resonance and noise decoupling. The hydrogen (^{1}H) and carbon (^{13}C) chemical shifts of samples as deuteriochloroform ($CDCl_3$) solutions are presented in parts per million (ppm) for internal tetramethylsilane (Me_4Si). ^{1}H NMR coupling patterns are designated as s = singlet, d = doublet, m = multiplet, q = quartet, t = triplet, dd = doublet of doublets.

Infrared spectra were obtained from samples as neat films and were recorded on Perkin-Elmer Model 257 and 421 spectrophometers with polystyrene (1601.4 cm^{-1}) as reference.

Gas-liquid partition chromatographic (GLC) analyses were performed on a Hewlett-Packard Model 5754B chromatograph interfaced with a Wang 600-T programmable calculator. GLC analyses were performed on samples dissolved in chloroform or benzene on 6 and 12 ft × 0.125 in. (i.d.) stainless steel columns with 5% and 10% XE-60 nitrile on Chromosorb W-HP-AW-DMCS (100–120 mesh) at 125–185 °C.

The mercaptans and chloroacetaldehyde dimethyl acetal were obtained from Aldrich Chemical Co. and Eastman Chemical and used without further purification. Sodium metaperiodate and potassium permanganate were obtained from Fisher Scientific Company.

Sulfides. All of the alkylthio derivatives were prepared in essentially the same manner and the procedure described for the methylthio derivative 1 below should be viewed as typical. We will refer to this procedure as method A.

Methylthioacetaldehyde Dimethyl Acetal (1). A solution of potassium methylthiolate was prepared by adding an ethanolic solution (150 mL) of methanethiol (19.2 g, 400 mmol) to an ethanolic solution (200 mL) of potassium hydroxide (25.8 g, 400 mmol). The solution was cooled to 0–5 °C (ice bath) and a solution of chloroacetaldehyde dimethyl acetal (50.0 g, 400 mmol) in 95% ethanol (100 mL) was added in one portion. The resulting solution was stirred at reflux for 4 h. The orange potassium chloride precipitate was removed and the filtrate was concentrated (rotary evaporator) to dryness. The resulting oil was dissolved in ether (150 mL), washed with water (2 × 100 mL), dried (magnesium sulfate), and concentrated (rotary evaporator) to give a red oil. Purification by vacuum distillation (0.25 torr) afforded a colorless oil (51.7 g, 85% yield): bp 32–34 °C; ^{1}H NMR ($CDCl_3$, 15% v/v) δ 4.45 (t, 1 H, J = 5.73 Hz, $(MeO)_2CH$), 3.36 (s, 6 H, $-OCH_3$), 2.64 (d, 2 H, J = 5.73 Hz, CH_2), 2.16 (s, 3 H, $-SCH_3$). Anal. Calcd for $C_5H_{12}SO_2$: C, 44.09; H, 8.88. Found: C, 44.16; H, 8.75.

Ethylthioacetaldehyde Dimethyl Acetal (4). The dimethyl acetal **4** was prepared in 94% yield (56.4g) by method A using ethanethiol (24.9 g, 400 mmol): bp 34–36 °C (0.075 torr); ^{1}H NMR ($CDCl_3$, 10% v/v) δ 4.43 (t, 1 H, J = 5.81 Hz, $(CH_3O)_2CH$), 3.35 (s, 6 H, OCH_3), 2.67 (d, 2 H, J = 5.81 Hz, SCH_2), 2.59 (q, 2 H, J = 7.21 Hz, CH_2), 1.24 (t, 3 H, J = 7.21 Hz, CH_3). Anal. Calcd for $C_6H_{14}SO_2$: C, 47.94; H, 9.39. Found: C, 47.77; H, 9.34.

Isopropylthioacetaldehyde Dimethyl Acetal (7). The dimethyl acetal **7** was synthesized in 92% yield (60.4 g) by method A using 2-propylthiol (25.8 g, 400 mmol): bp 43 °C (0.15 torr); ^{1}H NMR ($CDCl_3$, 15% v/v) δ 4.44 (t, 1 H, J = 5.86 Hz, $(CH_3O)_2CH$), 3.37 (s, 6 H, OCH_3), 2.87 (septet, 1 H, J = 7.12 Hz, $(CH_3)_2CH$), 2.71 (d, 2 H, J = 5.86 Hz, CH_2), 1.27 (d, 6 H, J = 7.12 Hz, CH_3). Anal. Calcd for $C_7H_{16}SO_2$: C, 51.18; H, 9.82. Found: C, 51.06; H, 9.94.

***tert*-Butylthioacetaldehyde Dimethyl Acetal (10).** The *tert*-butyl dimethyl acetal **10** was prepared according to method A in 93% yield (66.2 g) using *tert*-butyl mercaptan (3.61 g, 400 mmol): bp 47 °C (0.15 torr); ^{1}H NMR ($CDCl_3$, 9% v/v) δ 4.50 (t, 1 H, J = 6.1 Hz, $(CH_3O)_2CH$), 3.39 (s, 6 H, OCH_3), 2.75 (d, 2 H, J = 6.1 Hz, CH_2), 1.34 (s, 9 H, CH_3). Anal. Calcd for $C_8H_{18}SO_2$: C, 53.89; H, 10.18. Found: C, 53.99; H, 10.16.

Sulfoxides. The sulfinyl derivatives were all prepared by oxidation of the sulfide with sodium metaperiodate in a water–MeOH solution[8b] as described for the methyl sulfoxide **2** shown below. We will refer to this procedure as method B.

Methylthioacetaldehyde Dimethyl Acetal *S*-Oxide (2). A solution of sodium metaperiodate (10.7 g, 50.0 mmol) in water (100 mL) was added to a solution containing dimethyl acetal **1** (6.81 g, 50.0 mmol) and a 1:1 ratio of water–methanol for 16 h. The sodium iodate was removed by filtration and the resulting filtrate was extracted with chloroform (3 × 100 mL). The chloroform portions were combined, dried (anhydrous magnesium sulfate), and concentrated to dryness (rotary evaporator) to give a colorless oil. Purification by vacuum distillation (0.08 torr) gave **2** as a homogeneous liquid (6.84 g, 90% yield): bp 79 °C; ^{1}H NMR ($CDCl_3$, 8.1% v/v) δ 4.95 (t, 1 H, J = 5.78 Hz, $(CH_3O)_2CH$), 3.56 (s, 3 H, OCH_3), 3.51 (s, 3 H, OCH_3), 3.09 (d, 2 H, J = 5.78 Hz, CH_2), 2.72 (s, 3 H, SCH_3). Anal. Calcd for $C_5H_{12}SO_3$: C, 39.45; H, 7.95. Found: C, 39.34; H, 7.95.

Ethylthioacetaldehyde Dimethyl Acetal *S*-Oxide (5). Ethyl sulfoxide **5** was prepared in 90% yield (7.5 g) by method B using ethylthioacetaldehyde dimethyl acetal **4** (7.51 g, 50.0 mmol): bp 83 °C (0.08 torr); ^{1}H NMR ($CDCl_3$, 15% v/v) δ 4.77 (t, 1 H, J = 5.81 Hz, $(CH_3O)_2CH$), 3.43 (s, 3 H, OCH_3), 3.38 (s, 3 H, OCH_3), 2.93 (d, 2 H, J = 5.81 Hz, CH_2), 2.78 (q, 2 H, J = 7.09 Hz, CH_2CH_3), 1.33 (t, 3 H, J = 7.09 Hz, CH_3). Anal. Calcd for $C_6H_{14}SO_3$: C, 43.35; H, 8.49. Found: C, 43.16; H, 8.54.

Isopropylthioacetaldehyde Dimethyl Acetal *S*-Oxide (8). Dimethyl acetal *S*-oxide **8** was prepared in 88% yield (7.9 g) according to method B using acetal **7** (8.21 g, 50.0 mmol): bp 83–85 °C (0.08 torr); ^{1}H NMR ($CDCl_3$, 15% v/v) δ 4.78 (t, 1 H, J = 5.55, 6.22 Hz, $(CH_3O_2)CH$), 3.43 (s, OCH_3), 3.37 (s, 3 H, OCH_3), 2.82 (d, 1 H, J = 6.22 Hz, CH_2), 2.81 (d, 1 H, J = 5.55 Hz, CH_2), 2.75 (m, 1 H, CH), 1.28 (d, 3 H, J = 7.20 Hz, CH_3), 1.26 (d, 3 H, J = 7.12 Hz, CH_3). Anal. Calcd for $C_7H_{16}SO_3$: C, 46.64; H, 8.95. Found C, 46.52; H, 8.90.

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***tert*-Butylthioacetaldehyde Dimethyl Acetal *S*-Oxide (11).** Sulfoxide **11** was prepared in 92% yield (8.9 g) by method B using sulfide **10** (8.91 g, 50.0 mmol): bp 82–84 °C (0.06 torr); ^{1}H NMR ($CDCl_3$, 8.8% v/v) δ 4.79 (dd, 1 H, J = 4.75, 7.07 Hz, $(CH_3O)_2CH$), 3.46 (s, 3 H, OCH_3), 3.39 (s, 3 H, OCH_3), 2.72 (d, 1 H, J = 7.07 Hz, $S(O)CH_2$), 2.69 (d, 1 H, J = 4.75 Hz, $S(O)CH_2$), 1.25 (s, 9 H, CH_3). Anal. Calcd for $C_8H_{18}SO_3$: C, 49.43; H, 9.34. Found: C, 49.61; H, 9.28.

Sulfones. The sulfonyl derivatives were prepared using potassium permanganate in water[9] as described in the preparation of methyl sulfone **3**. This procedure will be referred to as method C.

Methylthioacetaldehyde Dimethyl Acetal *S,S*-Dioxide (3). A solution of sulfoxide **2** (3.04 g, 20.0 mmol) in 45 mL of water was added (1 h) to a solution of potassium permanganate (3.16 g, 50.0 mmol) in 100 mL of water at 25 °C. After 4 h, the solution was titrated with an aqueous solution of sodium metabisulfite. The resulting solution was extracted with chloroform (4 × 100 mL) and the combined organic layers were dried (anhydrous magnesium sulfate) and concentrated to dryness (rotary evaporator) to afford a colorless oil. Vacuum distillation under reduced pressure (0.08 torr) gave a homogeneous, colorless material (2.85 g, 85% yield): 82–84 °C; ^{1}H NMR ($CDCl_3$, 15% v/v) δ 4.78 (t, 1 H, J = 5.21 Hz, $(CH_3O)_2CH$), 3.36 (s, 6 H, CH_3O), 3.22 (d, 2 H, J = 5.21 Hz, CH_2), 2.91 (s, 3 H, SO_2CH_3). Anal. Calcd for $C_5H_{12}SO_4$: C, 35.70; H, 7.19. Found: C, 37.40; H, 7.50.

Ethylthioacetaldehyde Dimethyl Acetal *S,S*-Dioxide (6). Sulfone **6** was prepared in 87% yield (3.16 g) according to method C using sulfoxide **5** (3.31 g, 20.0 mmol): bp 84 °C (0.075 torr); ^{1}H NMR ($CDCl_3$, 12% v/v) δ 4.76 (t, 1 H, J = 5.80 Hz, $(CH_3O)_2CH$), 3.34 (s, 6 H, CH_3O), 3.16 (d, 2 H, J = 5.80 Hz, CH_2SO_2), 3.00 (q, 2 H, J = 7.6 Hz, SO_2CH_2), 1.30 (t, 3 H, J = 7.6 Hz, CH_3). Anal. Calcd for $C_6H_{14}SO_4$: C, 39.55; H, 7.74. Found C, 39.40; H, 7.70.

Isopropylthioacetaldehyde Dimethyl Acetal *S,S*-Dioxide (9). Sulfone **9** was synthesized in 93% yield (3.64 g) by method C using sulfoxide **8** (2.50 g, 13.0 mmol): bp 90 °C (0.12 torr); ^{1}H NMR ($CDCl_3$, 10% v/v) δ 4.77 (t, 1 H, J = 5.07 Hz, $(CH_3O)_2CH$), 3.33 (s, 6 H, CH_3O), 3.30 (m, 1 H, J = 6.92 Hz, $(CH_3)_2CH$), 3.17 (d, 2 H, J = 5.07 Hz, CH_2), 1.31 (d, 6 H, J = 6.92 Hz, CH_3). Anal. Calcd for $C_7H_{16}SO_4$: C, 42.82; H, 8.23. Found: C, 43.02; H, 8.30.

***tert*-Butylthioacetaldehyde Dimethyl Acetal *S,S*-Dioxide (12).** Sulfone **12** was prepared in 88% yield (3.69 g) by method C using sulfoxide **11** (3.89 g, 20.0 mmol): bp 104 °C (0.48 torr); ^{1}H NMR ($CDCl_3$, 15% v/v) δ 4.89 (t, 1 H, J = 4.83 Hz, $(CH_3O)_2CH$), 3.34 (s, 6 H, CH_3O), 3.12 (d, 2 H, J = 4.83 Hz, CH_2), 1.37 (s, 9 H, CH_3). Anal. Calcd for $C_8H_{18}SO_4$: C, 45.69; H, 8.63. Found: C, 45.66; H, 8.60.

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Effect of Increasing Electron Demand upon the Product-Determining Transition State in the Reaction of 4-Substituted 2-Nitrobenzenesulfenyl Chlorides and Benzenesulfenyl Chlorides with Bicyclo[2.2.1]hepta-2,5-diene

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The effect of increasing electron demand upon the product-determining transition state in the reaction of arenesulfenyl chlorides with bicyclo[2.2.1]hepta-2,5-diene has been investigated. As the electron-donating ability of the remote substituents on the phenyl ring of the sulfenyl chloride is varied from nitro to methoxy, the relative proportion of nortricyclene adduct is found to decrease relative to that of simple exo-anti addition. An ortho nitro group was found to lead to a stabilizing interaction only in the case of 2,4-dinitrobenzenesulfenyl chloride. A mechanism involving the competition of three neighboring-group effects is suggested, wherein the neighboring groups are respectively the 5,6 double bond of the substrate, the sulfur atom from the electrophile, and the ortho nitro substituent. In the first two cases the competition is with respect to the stabilization of positive charge at C-2. In the latter case the ortho nitro group is able to stabilize charge development on sulfur while the sulfur atom is itself acting as a neighboring group.

It is generally acknowledged that most changes in molecular structure which result in a change in neighboring-group participation also involve a change in the steric environment of the centers being studied. Evidence has, however, been provided that in certain cases, utilizing a series of molecules of essentially identical steric environment within the vicinity of the reactive sites, neighboring-group participation is a linear function of the electron demand of the incipient ionic species.[1] While such investigations have been traditionally involved with solvolytic behavior,[2] it seems apparent that the concept should apply equally well to electrophilic additions to carbon–carbon double bonds.

An example of such an application is readily found in the bromination of ring-substituted 1-phenylpropenes.[3] These additions are normally nonstereospecific, although

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