Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

Determination of the *Z* ^{1}H NMR chemical shift substituent parameters for the sulfinyl chloride and sulfinate ester functionalities

Jennifer S. O'Donnell; Robert J. Faragher; John M. Motto; Adrian L. Schwan

Online publication date: 13 May 2010

To cite this Article O'Donnell, Jennifer S. , Faragher, Robert J. , Motto, John M. and Schwan, Adrian L.(2004) 'Determination of the *Z* ^{1}H NMR chemical shift substituent parameters for the sulfinyl chloride and sulfinate ester functionalities', Journal of Sulfur Chemistry, 25: 1, 29 — 37
To link to this Article: DOI: 10.1080/17415990410001662383
URL: http://dx.doi.org/10.1080/17415990410001662383

J. Sulfur Chemistry, February 2004, Vol. 25, No. 1, pp. 29–37

Taylor & Francis
Taylor & Francis Group

RESEARCH ARTICLE

DETERMINATION OF THE *Z* ^{1}H NMR CHEMICAL SHIFT SUBSTITUENT PARAMETERS FOR THE SULFINYL CHLORIDE AND SULFINATE ESTER FUNCTIONALITIES

JENNIFER S. O'DONNELL, ROBERT J. FARAGHER, JOHN M. MOTTO and ADRIAN L. SCHWAN*

Guelph-Waterloo Centre for Graduate Work in Chemistry, Dept. of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada, N1G 2W1

(Received 21 October 2003; In final form 15 December 2003)

Using established and new ^{1}H NMR data for sulfinate esters and sulfinyl chlorides, the parameters required for predicting position-dependent alkene ^{1}H NMR chemical shifts of vinylic sulfinate esters and vinylic sulfinyl chlorides have been obtained. Standard deviations of the new *Z* parameters lie in the range 0.08 to 0.15 ppm. Sulfinyl chloride and cyclohexyl sulfinate derivatives of (*E*) and (*Z*)-2-cyanoethenesulfinic acids have been prepared for the first time.

Keywords: Sulfinyl chloride; Sulfinate; Chemical shift parameters; NMR

The alkene additivity chemical shift rule Eq. (1) has long been used by organic chemists to interpret ^{1}H NMR spectra [1–4]. When a double bond configuration is uncertain, application of the rule, using tabulated chemical shift influences of substituents (*Z* values) usually allows a rapid and tentative, if not unequivocal, assignment of double bond geometry.

$$\delta_{\mathrm{H}} = 5.25 + Z_{\mathrm{gem}} + Z_{\mathrm{cis}} + Z_{\mathrm{trans}} \tag{1}$$

Since its introduction [1], the table of substituent constants for common alkene substituents has found its way into several organic spectroscopy reference books. However, such entries are usually a reproduction of the original work [2–4], despite the emergence of new *Z* parameters for less common functional groups [5–8].

Sulfinyl chloride and sulfinate ester functional groups are part of modern investigations [9, 10] and, as such, double bonded compounds bearing these substituents are of interest to us [11–16] and to others [17–27]. Unfortunately the alkene additivity rule is unavailable for investigators in this area due to the lack of appropriate substituent constants.

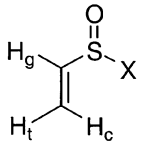
* Corresponding author. E-mail: schwan@uoguelph.ca

ISSN 1741-5993 print; ISSN 1741-6000 online
DOI: 10.1080/17415990410001662383

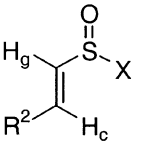
DETERMINATION OF *Z* PARAMETERS

We have compiled several ^{1}H NMR chemical shifts of protons on the double bond of α,β-unsaturated sulfinyl chlorides and sulfinate esters. A number of the compounds have been prepared previously in our group and were synthesized again for this specific purpose. Some sulfinate ester data has been taken from contributions of others. Nitrile substituted substrates **9** and **10** were prepared specifically for this study (*vide infra*).

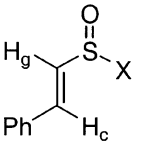
All of the compounds utilized here are indicated in Figure 1, where the accompanying reference(s) indicate the source of the data. For compounds such as **2b**, average chemical shift values were used for more than one compound. Chemical shift assignments of sulfinyl compounds **1**, **2**, **8** and **13**–**16** could be made unambiguously by analyzing chemical shifts and (or) coupling patterns. The pairs of vinylic hydrogens of species **3** and **5** were distinguished



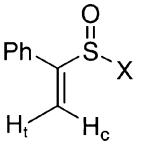
1a, X=Cl [14]
1b, X=OPP [14]
=OChol [13]



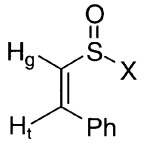
2a, X=Cl [14]
2b, X=OMe, R^2=Me [14]
=OEt, R^2=Me [23]
=OMe, R^2=*n*Hex [23]



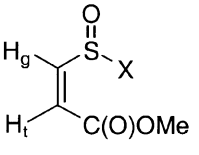
3a, X=Cl
3b, X=OPP [14]
=OChol [13]



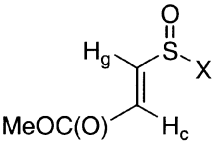
4a, X=Cl
4b, X=OPP [14]



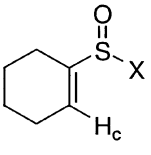
5a, X=Cl
5b, X=OPP [14]



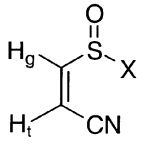
6a, X=Cl
6b, X=OEt [14]
= O*c*C_6H_{11} [14]



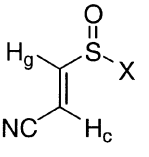
7a, X=Cl
7b, X=OEt [14]



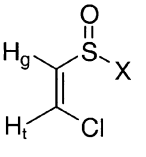
8a, X=Cl
8b, X=OPP [14]



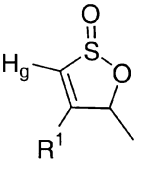
9a, X = Cl
9b, X = O*c*C_6H_{11}



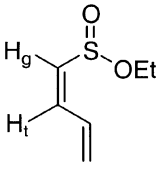
10a, X = Cl
10b, X = O*c*C_6H_{11}



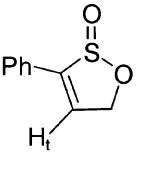
11a, X = Cl
11b, X = OPP [12]



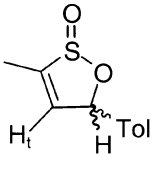
12, R^1 = Br [18]
13, R^1 = SMe [18]



14 [20]



15 [17]



16 [19]

FIGURE 1 Sulfinyl compounds employed for this determination (PP = 3-phenylpropyl; OChol = (−)-cholesteryl).

by the linewidths of their ^{1}H NMR resonances. Those vinylic hydrogens each appears as a doublet and one of the two doublets is broadened, a trait attributed to long-range coupling of the vinylic hydrogen and the aromatic ortho hydrogens. This afforded identification of the hydrogen nearer the aromatic ring. Using compound **5b**, this assignment was confirmed by a long-range COSY ^{1}H NMR experiment.

The hydrogens of sulfinyl compounds **4** were ascribed based on Gradient Selective Nuclear Overhauser Effect Spectroscopy (GOESY) [28] data. In each compound, irradiation of only one of the vinylic hydrogens caused enhancement of aromatic protons and that resonance was assigned to be cis to the aromatic group.

Nitrile compounds **9** and **10** have not been prepared previously. They were chosen as targets due to the known low Z substituent value for hydrogens positioned geminally to the nitrile group ($Z = 0.23$) [4]. Z_{gem} for a sulfoxide is 1.27 [29] and previous data indicate that the sulfinyl groups studied herein should be comparable [14], and since the Z constants for hydrogens β to the nitrile are greater than 0.23, it was felt that the chemical shift of vinylic hydrogens of compounds **9** and **10** would be readily differentiated. Furthermore, using the same arguments, the most downfield vinylic resonance could be confidently attributed to the hydrogen α to the sulfinyl group in **9** and **10**.

The hydrogens of compound **11b** could neither be differentiated nor confidently assigned, partially due to their close chemical shifts (6.64 *vs.* 6.53 ppm). However, by using some *a priori* knowledge of the sulfinate *vs.* sulfinyl chloride influences, a reliable assumption for **11a** could be made. Analyzing some of the assignments already established for compounds **1**–**5**, and noting a trend established previously [14], it is seen that the chemical shift of hydrogens geminal to the sulfinyl chloride are about 0.6 ppm downfield from the geminal hydrogen of the corresponding sulfinate ester. Conversely, the chemical shift differences of Z and E hydrogens between a sulfinyl chloride/sulfinate pair are about one-half the increment or less. Whereas the chemical shifts of the vinylic Hs of **11b** are close, there is a downfield shift to 7.24 ppm of one of the Hs of **11a**. The other H of **11a** only migrates to 6.84 ppm. On this basis, the most downfield H of **11a** is assigned to be α to the sulfinyl chloride.

For sulfinate ester **6b** (X = OEt), using GOESY analysis, irradiation of the methyl group of the ethyl sulfinate ester provided enhancement of only one vinylic hydrogen, which was attributed to be α to the sulfinate. For sulfinyl chloride **6a**, a ^{13}C NMR acquisition was performed without the typical broadband proton decoupling, an experiment that permits observation of proton coupling in the ^{13}C spectrum. The spectrum showed one vinylic carbon resonance to be broadened and of lesser intensity than the other. The origin of the broadening was ascribed to long-range (4 bond) coupling to the hydrogens of the methyl carboxylate and hence the two vinylic carbons of the compounds were differentiated. The hydrogens, correlated to the carbon resonances by an HSQC acquisition, were then assigned. An HMBC experiment corroborated the assignments. That acquisition allows a comparison of the magnitude of the $^2J_{^{13}C,^1H}$ and $^3J_{^{13}C,^1H}$ coupling constants of the carbonyl carbon to the α and β hydrogens, respectively. In keeping with the trends observed for simple acrylates as model compounds [30], the 3-bond coupling is larger in magnitude than the 2-bond coupling.

The hydrogens of sulfinate **7b** were determined in the same manner as for **6a**. However, we could find no spectroscopic means to assign the hydrogens of **7a**. For this sulfinyl chloride, we made the same assumption as for the **11b**/**11a** pair of compounds, *i.e.* the most downfield shifted resonance of **7a** compared with the chemicals shifts in **7b** is α to the sulfinyl group. The merit in this assumption can be confirmed by inspection of the proton resonances of **6a**/**6b**.

Given the series of hydrogen assignments, Tables I and II list the chemical shifts of the hydrogens and the calculated Z constant for the individual positions of the particular compounds. The Z values were obtained using Eq. (1), and established Zs for the other groups [4]

TABLE I Calculated individual Z values from sulfinyl chlorides.

Sulfinyl chloride	*Chemical shift*	*Calculated Z value*	*Sulfinyl chloride*	*Chemical shift*	*Calculated Z value*
1a	gem 7.24	1.99	**6a**[a]	gem 7.38	1.80
	cis 6.31	1.06		trans 6.38	0.45
	trans 6.12	0.87	**7a**[a]	gem 7.91	1.64
2a	gem 6.91	1.92		cis 6.77	0.84
	cis 6.72	1.03	**8a**	cis 6.72	1.06
3a	cis 7.74	1.14	**9a**	gem 7.65	1.82
	gem 7.24	1.62		trans 6.11	0.63
4a	cis 6.29	1.14	**10a**	gem 7.84	1.81
	trans 6.09	0.47		cis 6.47	0.99
5a	trans 7.17	0.57	**11a**	gem 7.24	1.96
	gem 7.06	1.91		trans 6.84	0.59

[a]The Z constants for conjugated structures were used for these compounds.

about the double bond were employed as required. Use of the 'conjugating' factor with carboxy esters **6** and **7** gave parameters in keeping with the others in Tables I and II. Conjugating parameters were not required with **14**.

The individual Z values of Tables I and II were then combined into like sets and average values were obtained (Table III). The values represent, for the first time, Z-substituent parameters for sulfinate ester and sulfinyl chloride functionalities. The parameters are accompanied by standard deviation (SD) values; SDs of 0.08 to 0.15 ppm are in line with those obtained for the SCN and NCS substituent parameters [6, 7], despite our using fewer sampling compounds.

TABLE II Calculated individual Z values from sulfinate esters.

Sulfinate ester	*Chemical shift*	*Calculated Z value*	*Sulfinate ester*	*Chemical shift*	*Calculated Z value*
1b	gem 6.65	1.40	**8b**	cis 6.51	0.85
	cis 6.12	0.87	**9b**	gem 7.13	1.30
	trans 5.96	0.71		trans 5.97	0.49
2b	gem 6.30	1.31	**10b**	gem 7.37	1.34
	cis 6.56	0.87		cis 6.27	0.79
3b	cis 7.28	0.68	**11b**[b]	– 6.64	–
	gem 6.89	1.27		– 6.53	–
4b	cis 6.17	1.02	**12**	gem 6.85	1.27
	trans 6.05	0.43	**13**	gem 6.15	1.21
5b	trans 7.10	0.50	**14**	gem 6.19	1.15
	gem 6.45	1.30		trans 6.69	0.46
6b[a]	gem 6.82	1.24	**15**	trans 7.05	0.76
	trans 6.31	0.38	**16**[c]	trans 6.30	0.64
7b[a]	gem 7.41	1.14			
	cis 6.58	0.65			

[a]The Z constants for conjugated structures were use for these compounds.
[b]The chemical shifts could not be differentiated.
[c]The chemical shift entry is an averaged value from a pair of stereoisomers.

TABLE III Z Parameters for sulfinyl compounds.

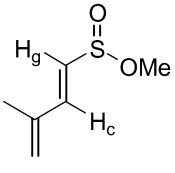
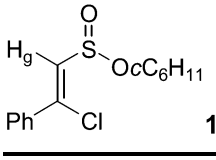
	Sulfinyl chloride		*Sulfinate ester*		
Position	*Average Z*	*SD*	*Average Z*	*SD*	*Sulfoxide*[a]
geminal	1.83	0.13	1.27	0.08	1.27
cis	1.04	0.10	0.82	0.13	0.67
trans	0.60	0.15	0.55	0.14	0.41

[a]Data taken from Ref. [29].

The values obtained clearly indicate that a sulfinyl chloride is a stronger electron-withdrawing group than the sulfinate ester. In both cases, Z decreases on going from geminal to the cis and trans positions, a trend that indicates the sulfinyl units are not as strong -R substituents as the carbonyl and nitrile functionalities. Comparing related sulfur functionalities, Z_{gem} for the sulfinate ester matches that for a sulfoxide (Table III). However, the Z_{cis} and Z_{trans} parameters suggest that the sulfoxide displays an attenuated net electron-withdrawing effect on the β-hydrogens compared with the sulfinate ester. The sulfinyl chloride functionality exerts a stronger influence on the geminal hydrogen than the sulfoxide or sulfone ($Z_{gem} = 1.58$) [4], but the sulfone has a stronger effect on the β-hydrogens ($Z_{cis} = 1.15$; $Z_{trans} = 0.95$) [4].

To demonstrate the usefulness of these new parameters, some otherwise unassignable vinylic resonances were sampled. Specifically, compounds **11b**, **17** and **18** were analyzed (Table IV). The data obtained in this paper allow assignment of the vinylic ^{1}H NMR resonances of **11b**. The data indicates that the hydrogen α to the Cl is the furthest downfield. Additionally, the published but unassigned vinylic ^{1}H NMR shifts of **17** can be assigned, as performed in the table. Finally, in a previous publication, we prepared **18** and inferred its double bond geometry mostly through mechanistic arguments, but with the assistance of NMR trends [14]. We are now more confident concerning the structure of **18** since calculations for both possible configurations, using the Z_{gem} parameter for sulfinate ester, favour our earlier structural assignment (Table IV).

TABLE IV Representative assignments with the new Z parameters.

Compound	*Hydrogens*	*Measured*	*Assignment*
11b	H_{gem} (calc) = 6.55 H_{trans} (calc) = 6.80	(6.53, 6.64)	H_{gem} = 6.53 H_{trans} = 6.64
 **17** [23]	H_{gem} (calc) = 6.48[a] H_{cis} (calc) = 7.05	(6.32, 7.00)	H_{gem} = 6.32 H_{cis} = 7.00
 **18** [12]	If Z as drawn: H_g (calc) = 6.92 if E config.: H_g (calc) = 6.61	7.14	**18** has Z configuration

[a]Conjugating parameters *not* used.

PREPARATION OF *E*- AND *Z*-2-CYANOETHENESULFINIC ACID DERIVATIVES

Access to sulfinyl chlorides **9a**/**10a** and sulfinates **9b**/**10b** was achieved by following the general procedures for the preparation of analogs **6a**/**7a** and **6b**/**7b** [14]. As indicated in Scheme 1, *p*-methoxybenzyl thiol (PMB-SH) was reacted with cyanoacetylene to afford a mixture of sulfides **19**, which was dominated by the presence of the *Z* isomer. To find complementary conditions favouring the *E*-isomer, several adaptations of the experimental conditions were explored. In no case could we find a significant change in the *E*:*Z* ratio.

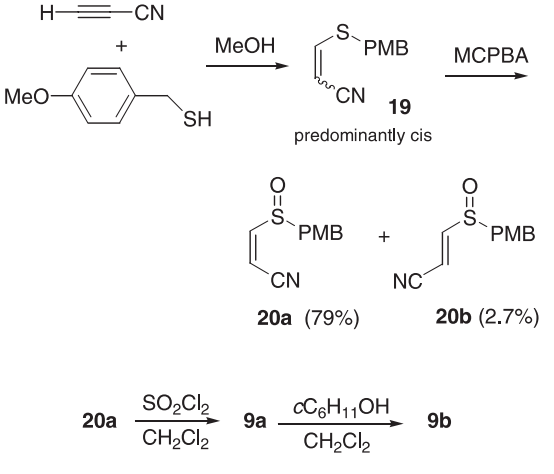
Sulfides **19** were carried forward with an MCPBA oxidation step. Sulfoxides possessing both double bond configurations were obtained. Isolation and purification *via* a chromatography/recrystallization sequence was straightforward. The sulfoxides were then subjected to oxidative fragmentation conditions to generate the sulfinyl chloride. A larger scale version of the reaction was performed to secure pure sulfinates as exemplified in Scheme 1 for **20a**, while the sulfinyl chlorides were pursued on a smaller scale.

EXPERIMENTAL

Preparation of Sulfoxides 20

To a round-bottom flask containing MeOH (25 mL) was added cyanoacetylene [31] (0.750 g, 13.2 mmol) and PMB-SH (1.94 g, 12.6 mmol). The resultant mixture was then cooled to 0 °C and Et_3N (1.34 g, 13.2 mmol) was added. This mixture was then stirred for 1 h and then quenched with saturated NH_4Cl(aq). Following extraction with EtOAc (3 × 10 mL), the combined organic components were then washed with brine, dried over $MgSO_4$ and evaporated *in vacuo* to yield *cis*- and *trans*-**19** as a yellow oil (2.38 g, 92%).

Sulfide mixture **19** (5.78 g, 28.2 mmol) and CH_2Cl_2 (100 mL) were added to a round-bottom flask and the mixture was cooled to −78 °C. Dried MCPBA (8.41 g, 70%, 28.2 mmol, 1 eq) dissolved in CH_2Cl_2 (140 mL) was added dropwise over 30 min. The so-obtained mixture was then stirred for 4 h, warmed to −30 °C and stirred overnight. Saturated Na_2CO_3(aq) (100 mL) was then added and the reaction was extracted with CH_2Cl_2 (3 × 50 mL). The combined organics were washed with saturated Na_2CO_3(aq) (100 mL) and brine, dried over $MgSO_4$ and



SCHEME 1

evaporated *in vacuo* to yield 7.8 g of **20** as a crude solid. The solid was chromatographed (silica gel, flash conditions, 30–100% EtOAc–hexanes) to yield sulfoxides **20a** and **20b** as separate fractions. Each fraction was separately recrystallized from hexanes–EtOAc to yield 168 mg (2.7%) of **20b** as a yellow solid (mp 99.5–100.5 °C) and 4.93 g (79%) of **20a** as a white solid (mp 103–104.5 °C).

Spectral data for **20a**: ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.20 (d, $J = 8.3$ Hz, 2H), 7.00 (d, $J = 10.8$ Hz, 1H), 6.91 (d, $J = 8.3$ Hz, 2H), 5.95 (d, $J = 10.8$ Hz, 1H), 4.16 (AB q, $J = 13.0$ Hz, $\Delta\delta = 37.3$ Hz, 2H), 3.81 (s, 3H); ^{13}C (100 MHz, $CDCl_3$), δ (ppm): 160.1, 155.6, 131.5, 119.4, 114.4, 112.6, 106.7, 59.5, 55.2; IR (neat) ν (cm^{-1}): 3040, 3010, 2962, 2937, 2840, 2243, 1611, 1584, 1513, 1441, 1304, 1255, 1179, 1104, 1053, 1035; MS (EI), m/z (%): 221 (M^+ (5)), 122 (22), 121 (100). Elemental analysis for $C_9H_{13}NO_2S$, calcd (%): C 59.70, H 5.01; found C 59.71, H 4.90.

Spectral data for **20b**: ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.45 (d, $J = 15.5$ Hz, 1H), 7.15 (d, $J = 7.6$ Hz, 2H), 6.92 (d, $J = 7.6$ Hz, 2H), 6.14 (d, $J = 15.5$ Hz, 1H), 4.10 (AB q, $J = 12.8$ Hz, $\Delta\delta = 12.9$ Hz, 2H), 3.82 (s, 3H); ^{13}C (100 MHz, $CDCl_3$), δ (ppm): 160.2, 155.0, 131.4, 119.1, 114.6, 114.5, 105.7, 59.3, 55.3; IR (neat) ν (cm^{-1}): 3066, 3039, 2969, 2916, 2838, 2229, 1610, 1514, 1253, 1178, 1106, 1056, 1032; MS (EI), m/z (%): 221 (M^+ (1)), 122 (10), 121 (100). Elemental analysis for $C_9H_{13}NO_2S$, calcd (%): C 59.70, H 5.01; found C 59.66, H 4.83.

Preparation of Sulfinate Ester 9b

To a flame-dried round-bottom flask was added sulfoxide **20a** (408 mg, 1.84 mmol) and CH_2Cl_2 (40 mL). The resultant mixture was the cooled to −78 °C and SO_2Cl_2 (2.21 mL, 2.21 mmol, 1.0 M solution, 1.2 eq) was added dropwise followed by stirring for 15 min, after which time the bath was removed and the solution allowed to warm to room temperature. After stirring for a further 2 h, the mixture was cooled to −78 °C and quenched with cyclohexanol (155 μL, 1.47 mmol, 0.8 eq) and K_2CO_3 (1.27 g, 9.22 mmol, 5 eq). The mixture was the allowed to warm to room temperature overnight before it was filtered through Celite® and evaporated *in vacuo* to yield a yellow oil. Flash chromatography (2 columns: 20% EtOAc–hexanes; then CH_2Cl_2) yielded **9b** as a white solid, mp 42.5–43.5 °C (153 mg, 41.6%). Data for **9b**: ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.13 (d, $J = 10.9$ Hz, 1H), 5.97 (d, $J = 10.9$ Hz, 1H), 4.40 (dddd (apparent tt), $J = 3.9$ & 5.2 Hz, 1H), 2.00 (m, 2H), 1.80–1.76 (m, 2H)), 1.66–1.53 (m, 3H), 1.42–1.21 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 157.5, 112.6, 105.4, 80.7, 33.7, 33.1, 24.9, 23.7, 23.6; IR (neat) ν (cm^{-1}): 3043, 2938, 2861, 2228, 1684, 1453, 1218, 1131, 1056. Elemental analysis for $C_9H_{13}NO_2S$, calcd (%): C 54.25, H 6.58; found: C 54.12, H 6.40.

Analytical Preparation of Sulfinyl Chloride 9a

To a flame-dried round-bottom flask was added sulfoxide **20a** (75.0 mg, 0.339 mmol) and CH_2Cl_2 (6 mL) and the resultant mixture was cooled to −78 °C. SO_2Cl_2 (0.440 mL, 0.440 mmol, 1.0 M solution, 1.3 eq) was then added dropwise and the mixture was stirred for 1 h, after which time the bath was removed and the solution was allowed to warm to room temperature. After 3 hours at room temperature, an aliquot of the mixture was removed for IR and ^{1}H NMR analysis of **9a**. Spectral data for **9a**: ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.65 (d, $J = 10.5$ Hz, 1H), 6.11 (d, $J = 10.5$ Hz, 1H); IR (neat) ν 1144 (S=O) cm^{-1}. To confirm the structure of **9a**, the remainder of the mixture was cooled to −78 °C, quenched with cyclohexanol (36 μL, 0.339 mmol, 1 eq) and K_2CO_3 (234 mg, 1.69 mmol, 5 eq) and then allowed to warm to room temperature overnight. The mixture was then filtered through Celite® and evaporated *in vacuo* to yield **9b** as a yellow oil.

Preparation of Sulfinate Ester 10b

As for **9b**, a reaction was set up at −78 °C using sulfoxide **20b** (145.7 mg, 0.659 mmol) in CH_2Cl_2 (10 mL) and SO_2Cl_2 (0.850 mL, 0.850 mmol, 1.0 M solution, 1.3 eq). After stirring for 4 h at room temperature, the mixture was recooled to −78 °C and quenched with cyclohexanol (70 μL, 0.659 mmol, 1 eq) and K_2CO_3 (455 mg, 3.29 mmol, 5 eq) and then allowed to warm to room temperature overnight. Workup as for **9b** above gave crude **10b**, which was subjected to flash chromatography (20% EtOAc–hexanes) to yield **10b** as a clear oil (110 mg, 84%). Spectral data for **10b**: ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.37 (d, J = 15.8 Hz, 1H), 6.27 (d, J = 15.8 Hz, 1H), 4.30 (dddd (apparent tt), J = 3.9 & 5.2 Hz, 1H), 1.92–1.89 (m, 2H), 1.76–1.72 (m, 2H), 1.66–1.48 (m, 3H), 1.38–1.18 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 155.3, 114.2, 107.8, 80.1, 33.4, 33.3, 29.5, 24.8, 23.6, 23.5; IR (neat) ν (cm^{-1}): 3048, 2936, 2859, 2230, 1451, 1370, 1191, 1134, 1033. Elemental analysis for $C_9H_{13}NO_2S$, calcd (%): C 54.25, H 6.58; found: C 54.32, H 6.44.

Analytical Preparation of Sulfinyl Chloride 10a

As for **9a**, a reaction was set up using sulfoxide **20b** (65.2 mg, 0.295 mmol) in $CDCl_3$ (4 mL) and SO_2Cl_2 (0.354 mL, 0.354 mmol, 1.0 M solution, 1.2 eq). After 15 min at −78 °C the bath was removed and the solution was allowed to warm to room temperature. After 10 h at room temperature, 1 h at 35 °C then cooling, IR and ^{1}H NMR of **10a** were obtained. Spectral data for **10a**: ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.53 (d, J = 15.4 Hz, 1H), 6.61 (d, 15.4 Hz, 1H); IR ($CDCl_3$): ν 1144 (S=O) cm^{-1}. To confirm the structure of **10a**, the mixture was then cooled to −78 °C, quenched with cyclohexanol (23 μL, 0.236 mmol, 0.8 eq) and K_2CO_3 (204 mg, 1.48 mmol, 5 eq) and allowed to warm to room temperature overnight. The resultant mixture was then filtered through Celite® and evaporated *in vacuo*, yielding a **10b** as a yellow oil.

General Procedure for Acquisition of Sulfinyl Chloride NMR Data

As indicated for the analytical production of **9a** and **10a**, PMB, DPM [14] or 2-trimethylsilylethyl [12] sulfoxides, stirring in CH_2Cl_2 or $CDCl_3$, were subjected to SO_2Cl_2 treatment at −78 °C. After warming, the $CDCl_3$ solutions were analyzed directly on a Bruker Avance spectrometer operating at either 400 or 600 MHz for ^{1}H NMR acquisitions. CH_2Cl_2 solutions were concentrated under dry conditions and the residue taken up in $CDCl_3$ for analysis.

Acknowledgements

The authors thank NSERC of Canada for funding and Professor Glenn Penner and Ms Valerie Robertson for providing assistance with structure determinations and NMR pulse sequences.

References

[1] Pascual, C., Meier, J. and Simon, W., *Helv. Chim. Acta*, **49**, 164 (1966).
[2] Pavia, D. L., Lampman, G. M. and Kriz, G. S., *Introduction to Spectroscopy; A Guide for Students of Organic Chemistry* (Harcourt College Publishers, Orlando, 2001), 3rd ed., p. A-18.
[3] Lambert, J. B., Shurvell, H. F., Lightner, D. A. and Cooks, R. G., *Organic Structural Spectroscopy* (Prentice-Hall, Upper Saddle River, 1998), p. 44.
[4] Silverstein, R. M. and Webster, F. X., *Spectroscopic Identification of Organic Compounds* (J. Wiley and Sons, New York, 1998), 6th ed., p. 206.
[5] Matter, U. E., Pascual, C., Pretsch, E., Pross, A., Simon, W. and Sternhell, S., *Tetrahedron*, **25**, 691 (1969).

[6] Guy, R. G., *Magn. Reson. Chem.*, **26**, 488 (1988).
[7] Guy, R. G., *Magn. Reson. Chem.*, **26**, 967 (1988).
[8] Zyablikova, T. A., Khusainova, N. G. and Cherkasov, R. A., *Russ. J. Gen. Chem.*, **67**, 1414 (1997).
[9] Schwan, A. L. and Strickler, R. R., *Org. Prep. Proced. Int.*, **31**, 579 (1999).
[10] Allin, S. M., In: Page, P. (Ed.), *Organosulfur Chemistry, Vol. 2: Synthetic and Stereochemical Aspects* (Academic Press, San Diego, 1998), Chap. 2.
[11] Strickler, R. R., Motto, J. M., Humber, C. C. and Schwan, A. L., *Can. J. Chem.*, **81**, 423 (2003).
[12] Schwan, A. L., Strickler, R. R., Dunn-Dufault, R. and Brillon, D., *Eur. J. Org. Chem.*, 1643 (2001).
[13] Strickler, R. R. and Schwan, A. L., *Tetrahedron: Asymmetry*, **11**, 4843 (2000).
[14] Schwan, A. L., Strickler, R. R., Lear, Y., Kalin, M. L., Rietveld, T. E., Xiang, T.-J. and Brillon, D., *J. Org. Chem.*, **63**, 7825 (1998).
[15] Schwan, A. L., Snelgrove, J. L., Kalin, M. L., Froese, R. D. J. and Morokuma, K., *Org. Lett.*, **1**, 487 (1999).
[16] Lear, Y. and Schwan, A. L., *J. Org. Chem.*, **64**, 8138 (1999).
[17] Thoumazeau, E., Jousseaume, B., Tiffon, F. and Duboudin, J. G., *Heterocycles*, **19**, 2247 (1982).
[18] Braverman, S. and Duar, Y., *J. Am. Chem. Soc.*, **105**, 1061 (1983).
[19] Baudin, J.-B., Julia, S. A., Ruel, O., Toupet, L. and Wang, Y., *Bull. Soc. Chim. Fr.*, **132**, 79 (1995).
[20] Crumbie, R. L. and Ridley, D. D., *Aust. J. Chem.*, **34**, 1017 (1981).
[21] Lonchambon, G., Delacroix, A., Garreau, R., Veltz, J. N. and Petit, J., *Bull. Soc. Chim. Fr.*, 541 (1979).
[22] Niestroj, M., Neumann, W. P. and Mitchell, T. N., *J. Organomet. Chem.*, **519**, 45 (1996).
[23] Baudin, J.-B., Julia, S. A. and Wang, Y., *Bull. Soc. Chim. Fr.*, **132**, 952 (1995).
[24] Braverman, S. and Reisman, D., *J. Am. Chem. Soc.*, **99**, 605 (1977).
[25] Hurley, A. L., Welker, M. E. and Day, C. S., *J. Organomet. Chem.*, **598**, 150 (2000).
[26] Van der Leij, M., Strijtveen, H. J. M. and Zwanenburg, B., *Rec. Trav. Chim. Pays-Bas*, **99**, 45 (1980).
[27] Chan, W. H., Lee, A. W. M. and Lee, K. M., *J. Chem. Res. (S)*, 138 (1994).
[28] Stonehouse, J., Adell, P., Keeler, J. and Shaka, A. J., *J. Am. Chem. Soc.*, **116**, 6037 (1994).
[29] Pretsch, E., Buhlman, P. and Affolter, C., *Structure Determination of Organic Compounds* (Springer, Berlin, 2000), pp. 172–173.
[30] Marshall, J. L., Miller, D. E., Conn, S. A., Seiwell, R. and Ihrig, A. M., *Acc. Chem. Res.*, **7**, 333 (1974).
[31] Jung, M. E. and Buszek, K. R., *J. Am. Chem. Soc.*, **110**, 3965 (1988).