Preparation of 4-Substituted Benzyl Sulfoxylates and Related Chemistry

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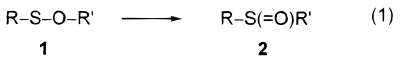
Preparation of dibenzyl sulfoxylate **7a** and 4-substituted benzyl sulfoxylates (**7b**, 4-NO_2; **7c**, 4-Cl; **7d**, 4-CH_3O, **7e**: 4-CH_3) are reported. The unexpected stability of **7b** has permitted the first X-ray determination at room temperature of a sulfoxylate. The thermal isomerization of sulfoxylates **7b**−**c** to sulfinates **8b**−**c** was studied in different solvents (toluene-d_8, $CDCl_3$, and CD_3CN) and interpreted as a concerted unimolecular process following first-order kinetics.

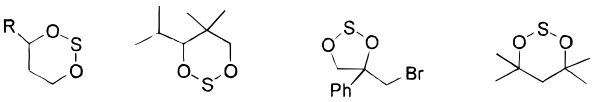
Introduction

The chemistry related to the rearrangement of alkyl, aryl, and allyl sulfenates **1** to their corresponding sulfoxides **2** has been reviewed by Braverman (eq 1).[1a] The



thermal sulfenate−sulfoxide interconversion for benzyl arylsulfenates, Ar−CH_2−O−S−Ar, to their sulfoxides, Ar−CH_2−S(═O)Ar, is believed to occur via a concerted intramolecular mechanism (Scheme 1).[1b]

Analogously, Thompson noted that dibenzyl sulfoxylate, $(PhCH_2O)_2S$, rearranges to the benzyl α-toluenesulfinate, $PhCH_2S(=O)OCH_2Ph$, during preparation.[2] Several linear sulfoxylates were prepared by Thompson in good yield (R = R′ = *n*-Pr, 62%; *i*-Pr, 67%; *n*-Bu, 70%; *n*-C_5H_{11}, 56%; cholesteryl, 16%).[2] In that same paper, some cyclic sulfoxylates were also reported with their yields (**3a**, 20%; **3b**, 8%; **4**, 58%). Sulfoxylates **5**[3a] and **6**[3b,c] were claimed but no yields were reported.



Contrary to Thompson's preliminary work on sulfoxylates, we have found that 4-substituted benzyl sulfoxylates **7a**−**e** could be isolated and were not that prone to readily rearrange to their corresponding sulfinates **8a**−**e**. Thermal isomerization studies have shown that

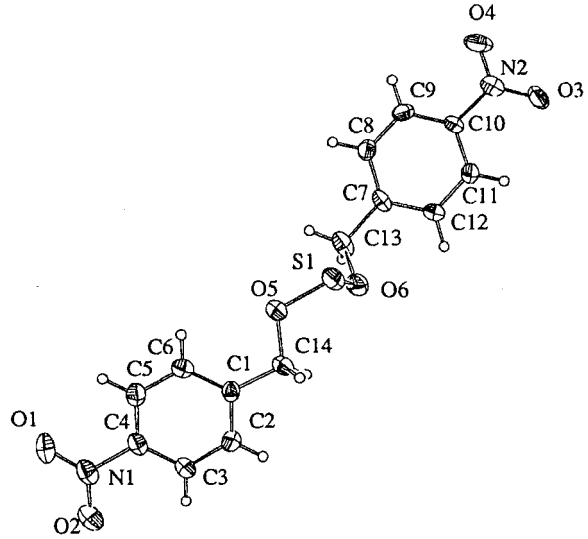
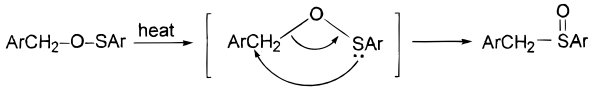


Figure 1. ORTEP drawing of bis(4-nitrobenzyl) sulfoxylate **7b**.

Scheme 1



the nature of the *para* substituent on the benzene ring is important in relation of the stability of sulfoxylates **7a**−**e**. The above proposal was verified by the obtention of suitable crystals for the X-ray determination of **7b**.

Results and Discussion

Sulfoxylates **7a**−**e** were prepared by adding a solution of sulfur dichloride, SCl_2 (1 equiv), to a solution of the corresponding benzyl alcohol (2 equiv) in the presence of triethylamine, Et_3N (2 equiv), at −78 °C. However, SCl_2 is prone to decomposition and gives sulfur monochloride, S_2Cl_2, even at low temperature (eq 2). In the present

(1) (a) Braverman S. *The Chemistry of Sulfones and Sulfoxides*; Patai, S., Rappoport, Z., Sterling, C. J. M., Eds.; Wiley: Chichester, 1988; Chapter 14. (b) Kice J. L. *Adv. Phys. Org. Chem.* **1980**, 100.

(2) Thompson Q. E. *J. Org. Chem.* **1965**, *30*, 2703.

(3) (a) Kogami H.; Motoki S. *J. Org. Chem.* **1978**, *43*, 1262. (b) Chapman J. S.; Cooper J. W.; Roberts B. P. *J. Chem. Soc., Chem. Commun.* **1976**, 835. (c) Birkofer L.; Niedrig H. *Chem. Ber.* **1966**, *99*, 2070.

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Table 1. Product Distribution[a] for the Preparation of 4-Substituted Benzyl Sulfoxylates 7a−e

ROH[b] **11**	RO(S=O)R **8**	$(RO)_2S$=O **10**	ROSSOR **9**	ROSOR **7**	exptl conditions[d] (°C)
b[f]				10	0−5
b	9	15	26	27	−10
b		16	15	50	−40
b		11	10	58	−78
e	7	23	18	21	−40
d[c]	4	34	24	*e*	−40
a		16	22	27	−78
a		25	26	24	−40
c		17	17	46	−78
c	3	24	19	38	−40

[a] % yield. [b] R = 4-X−$C_6H_4CH_2$: **11a**, X = H; **b**, X = NO_2; **c**, X = Cl; **d**, X = OMe; **e**, X = Me. [c] NMR yields otherwise isolated yields using column chromatography. [d] 2 h, solvent CH_2Cl_2. [e] Compound was formed (NMR) but does not withstand column chromatography on silica gel. [f] Product precipitated from the mixture in the fridge.

$$\left[2\,SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2\right] \xrightarrow[\text{heat}]{PCl_5} 2\,SCl_2 + PCl_3 \quad (2)$$

preparation, the decomposition to S_2Cl_2 was minimized due to the low temperature used for the reaction. However, the product distribution reported in Table 1 shows formation of the corresponding dialkoxy disulfides **9a**−**e**,[4] sulfites **10a**−**e**,[4] sulfinates **8a**−**e**, and unreacted alcohols **11a**−**e**.

The formation of **7b** was enhanced at the expense of the formation **9b** as the reaction temperature was lowered. This is attributed to the slowing of the rate of disproportionation of SCl_2 to S_2Cl_2. The formation of sulfite **10b** can be rationalized considering the "oxychloro-sulfide and disulfide" types of intermediates **12** and **13**; they are known to decompose to the sulfite at −78 °C (eqs 3−5).[5] Intermediate **12** may also be gener-

$$ROSSOR + SCl_2 \longrightarrow \underset{\mathbf{12}}{[ROSCl]} + \underset{\mathbf{13}}{[ROSSCl]} \quad (3)$$

$$3\,\underset{\mathbf{12}}{[ROSCl]} \xrightarrow[-78\,^\circ C]{} (RO)_2S{=}O + RCl + S_2Cl_2 \quad (4)$$

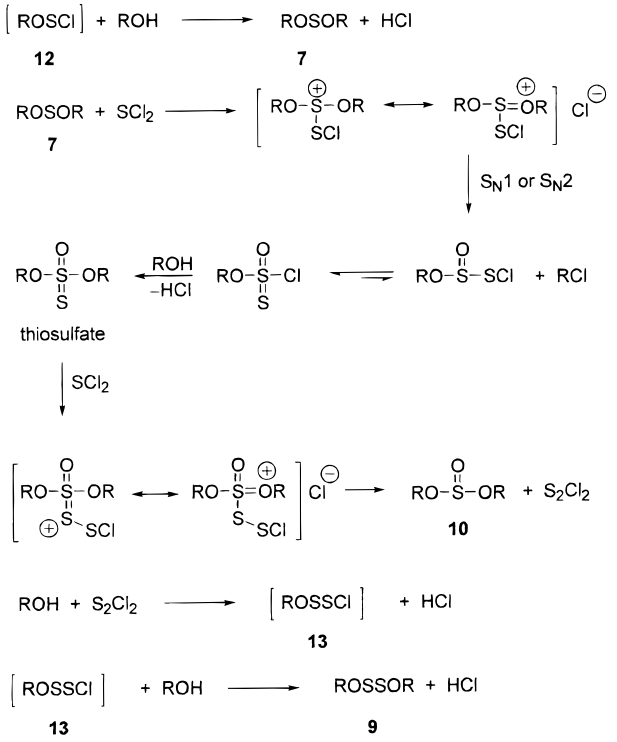
$$3\,\underset{\mathbf{13}}{[ROSSCl]} \xrightarrow[\text{slow}]{} \underset{\mathbf{10}}{(RO)_2S{=}O} + RCl + S_2Cl_2 + 3/8\,S_8 \quad (5)$$

ated at very low temperature (eq 6) and leads to the formation of sulfite **10** following Scheme 2. The formation of dialkoxy disulfide **9b** seems to be unavoidable considering the multiple sources of S_2Cl_2 (eqs 4 and 5 and Scheme 2) even at low temperature.

$$ROH + SCl_2 \longrightarrow \underset{\mathbf{12}}{[ROSCl]} + HCl \quad (6)$$

Interestingly, **9b** and **10b** were detected in a separate experiment where sulfoxylate **7b** was treated with SCl_2 (1 equiv) under the same experimental conditions (−78 °C followed by workup at 0 °C). A potential rationale for their formation could follow Scheme 2, since **9b** and **10b** were formed and detected during the course of the reaction prior to the workup. Although 4-nitrobenzyl chloride was not detected, it is of interest that the formation of the sulfite in this reaction has, to our knowledge, not been previously rationalized.

Scheme 2



Sulfoxylates **7** could be isolated and were stable to rearrangement to the corresponding sulfinates **8** when purified. It seems that the presence of HCl and intermediates **12** and **13** generated in the reaction mixture are responsible for the wide product distribution observed. Nevertheless, the low temperature is a key factor for the preparation of the 4-substituted benzyl sulfoxylates. Once purified, **7b** and **7c** could be recrystallized. In the case of **7b**, the crystals were suitable for X-ray analysis at room temperature and a full determination was obtained (see Experimental Section). Sulfoxylates **7a** and **7e** were able to withstand column chromatography conditions, and samples were isolated and found to isomerize in an hour once purified at ambient temperature. Where **7d** was only detected by NMR in the reaction mixture, **7b** and **7c** were stable enough, once purified, to be kept at −30 °C under N_2 in the freezer over a period of 2 months.

Sulfoxylate **7b** and **7c** were found to rearrange slowly in $CDCl_3$ over a period of time not exceeding 24 and 35 h, respectively (for **7b**: Figure 2). The isomerization process for **7b** and **7c** was studied in solution (0.13−0.14 M) at temperatures close to room temperature. The kinetic runs, in deuterated solvent, were found to obey first-order kinetics. The process was monitored in three different solvents at different temperatures (**7c** in toluene-d_8 at 19.9, 25.0, and 27.3 °C; **7b** in toluene-d_8 at 19.9, 25.0, 27.3, and 35.3 °C; **7b** in $CDCl_3$ at 19.9, 20.3, 25.0, 27.2, and 35.3 °C; **7b** in CD_3CN at 19.9, 25.0, 27.3, and 35.2 °C) and each run was duplicated; in certain cases, 3−4 repetitions were carried out. The kinetics of the

(4) (a) Tardif S. L.; Rys A.; Abrams C. B.; Abu-Yousef, I. A.; Lesté-Lasserre, P. B. F.; Schultz, E. K. V.; Harpp, D. N. *Tetrahedron* **1997**, *53*, 12225. (b) Tardif, S. L.; Williams, C. R.; Harpp, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 9067. (c) Thompson, Q. E.; Crutchfield, M. M.; Dietrich, M. M.; Pierron, E. *J. Org. Chem.* **1965**, *30*, 2692.

(5) Schmidt H.; Steudel R. *Z. Naturforsch.* **1990**, *45B*, 557: R = *i*-Pr; ROSSOR reacts with SCl_2 at −78 °C to give intermediates **12** and **13** that decompose to give the sulfite (eq 3). While the intermediate **12** decomposes rapidly at −78 °C, the intermediate **13** was detected and analysed at −20 °C.

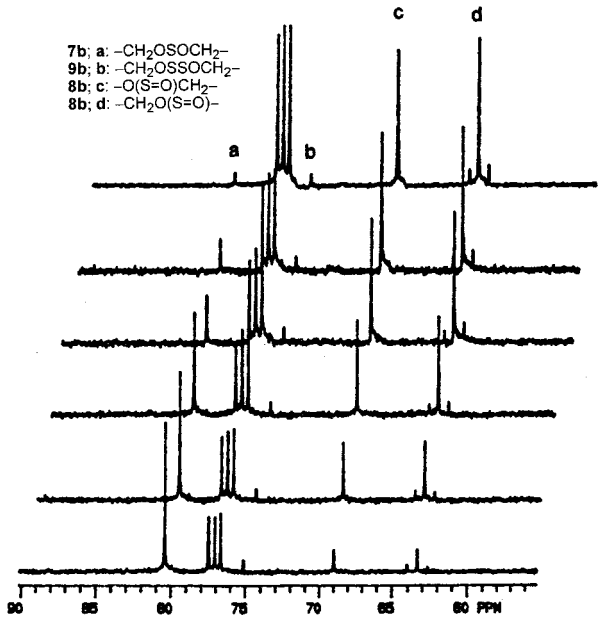


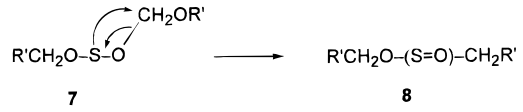
Figure 2. Isomerization of **7b** to **8b** in $CDCl_3$ at 20.3 °C; from bottom to top 1.9, 5.6, 9.3, 13.0, 16.8, and 22.4 h, respectively.

Table 2. ^{13}C NMR Chemical Shifts[a] for 7b,c and 8b,c

solvent[b,c] μ (D) ϵ	δ_C (CH_2)		$\delta_{C\alpha}$ (CH_2)[d] $\delta_{C\alpha'}$ (CH_2)[d]	
	7b	**7c**	**8b**	**8c**
toluene-d_8	80.37	81.07	67.81	68.47
0.36			63.31	63.58
2.38				
chloroform-*d*	80.33	81.06	68.90	69.71
1.01			63.26	63.55
4.81				
acetonitrile-d_3	81.61	81.88	69.62	69.93
3.92			63.49	63.40
35.94				

[a] In ppm at 19.6−20.3 °C. [b] Dipole moment μ (Debye) and dielectric constant ϵ at 25 °C. [c] Reference 6. [d] Cα and Cα′ are on the left and right hand side of O(S=O) functionality, respectively.

Scheme 3



intensity change of the ^{13}C NMR signal of the benzylic methylene carbon were followed. The average correlation coefficient for all the rate constant plots is 0.994. ^{13}C chemical shifts for the sulfoxylates **7b**,**c** and sulfinates **8b**,**c** in these different solvents are reported in Table 2.

The isomerization process is unimolecular; the central sulfur atom acts as an electron donor, interacting with the adjacent benzylic carbon as this atom is loosening its CH_2−O interaction to the profit of the forming sulfonyl group (S=O) (Scheme 3). This concerted three-membered ring transition state is in reasonable agreement with both kinetic and thermodynamic parameters correlated in Table 3: the positive activation enthalpies and the negative entropies (except for **7b** in CD_3CN, vide infra) are comparable to other pericyclic concerted processes[7c] such as the Diels−Alder reactions and the Cope rearrangement. The entropy factor, at least for **7b** in toluene-d_8 and in $CDCl_3$, is interpreted in terms of restricted internal rotation to achieve the activated complex in the transition state. The activation parameters can be qualitatively interpreted. The activation energy of **7b** was increased in CD_3CN from the less polar solvents $CDCl_3$ and toluene-d_8, likely due to an increase of solute−solvent interaction and the polar interaction between the nitro group of **7b** and the cyano group of acetonitrile.[6] The entropy of activation for these reactions is generally consistent with transition states for unimolecular process. That there appears to be a more ordered transition state required (more negative $\Delta S^{\ddagger}$) for the less polar solvents is reasonable. The values of k_{rel} indicate that the change of solvent polarity has a very small effect on the rate of the reaction and that the charge distribution in the activated complex of **7b** is very similar to **7b** itself (isopolar activated complex).[7]

Table 3. Relative Rates and Activation Parameters[a,b] for Isomerization 7b,c to 8b,c

7	solvent	$k \times 10^{-6}$ [a] (s^{-1})	k_{rel}	E_a	ln *A*	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$ (eu)
b	toluene-d_8	43.0	1.0	21.1 ± 0.3	26.1	23.4	−10.1 ± 0.9
	$CDCl_3$	57.8	1.3	19.9 ± 0.2	24.4	23.0	−12.6 ± 0.8
	CD_3CN	52.9	1.2	25.1 ± 0.5	33.2	22.8	5.7 ± 0.9
c	toluene-d_8	14.5	1.0	26.2 ± 0.7	33.9	23.6	6.8 ± 1.1
	$CDCl_3$	24.4	1.7				
	CD_3CN	19.1	1.3				

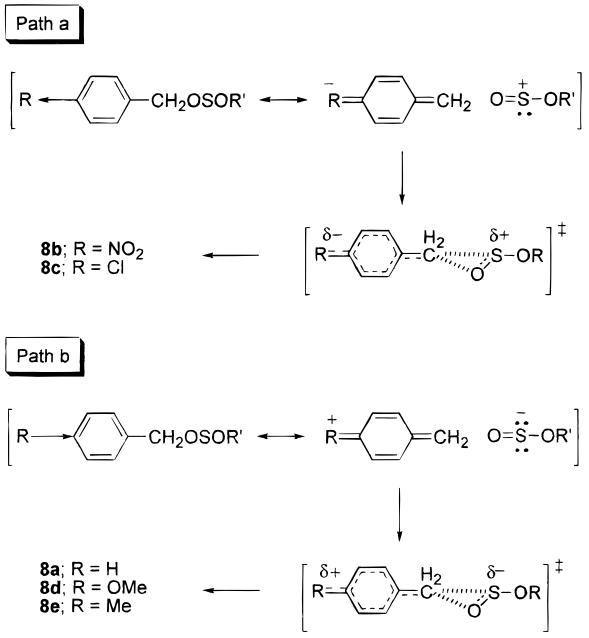
[a] At 19.9 °C; E_a and $\Delta G^{\ddagger}$ are expressed in kcal mol^{-1}, and error limits represent the standard deviation. [b] Temperature dependence of *k* for **7b** was not studied in $CDCl_3$ and CD_3CN.

Although the concerted mechanism of isomerization is reasonable, an intimate or tight ion-pair, as well as radical-pair, cannot be completely ruled out in the transition state. The stability and reactivity observed among the sulfoxylates **7a**−**e** can be qualitatively explained in terms of valence bond structures leading to a tight ion-pair in the transition state (Scheme 4). Sulfoxylates **7b**,**c** are more stable in comparison to **7a**,**d**−**e** presumably because **7b**,**c** have an electronegative group in the *para* position causing the ring to be electron deficient and to the extreme formation of a tight ion-pair containing the cation $R'OS^{+}(=O)$ (Scheme 4, path a). The isomerization of **7** via the concerted process or the tight ion-pair where the sulfur from the O−S−O functionality acts as a donor would be predicted to be slowed when the electron withdrawing groups are attached at the *para* position. This also rationalizes why **7a**,**d**−**e** were found to isomerize at room temperature in a matter of an hour and less. In **7d**, the resonance electron-donating effect outweighs the possible inductive electron-withdrawal effect of the moderate electronegative oxygen atom of the methoxy group leading to the possible formation of a tight ion-pair containing the more favorable anion $R'OS^{-}(=O)$ that undergoes rapid recombination (Scheme 4, path b). The contribution of the more stable anion $R'OS^{-}(=O)$ over the cation $R'OS^{+}(=O)$ might favor a dissociative mechanism for **7a**,**d**,**e**. Similar mechanistic considerations were reported to be substrate-dependent. The thermal sulfenate−sulfoxide rearrangement of allyl and

(6) Reichardt C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd revised Ed.; VCH: Weinheim, 1990.

(7) (a) Pacey, P. D. *J. Chem. Educ.* **1981**, *58*, 612. (b) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley: New York, 1981. (c) Snyder, J. P.; Harpp, D. N. *J. Am. Chem. Soc.* **1976**, *98*, 7821. (d) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1968. (e) Breslow, R. *Organic Reaction Mechanism An Introduction*; W. A. Benjamin Inc.: New York, 1965.

Scheme 4



propargyl sulfenates is reported to proceed by a facile [2,3]-sigmatropic shift;[9a] *p*-methoxybenzyl trichloromethanesulfenate is believed to undergo thermal rearrangement to the corresponding sulfoxide, in hexane, via a dissociative mechanism ($k = 3.4 \times 10^{-4}$ s^{-1} at 77 °C, $\Delta H^{\ddagger} = 28$ kcal/mol, $\Delta S^{\ddagger} = 5$ eu).[9b] The rearrangement of benzyl *p*-toluenesulfenate to the corresponding sulfoxide, in benzene, is established to proceed by a concerted intramolecular mechanism ($k = 8.7 \times 10^{-5}$ s^{-1} at 120 °C, $\Delta H^{\ddagger} = 29.7$ kcal/mol, $\Delta S^{\ddagger} = -2$ eu).[9c] The transition state calculations for the concerted conversion of dimethyl sulfenate to dimethyl sulfoxide is expected to be about 21 kcal/mol above the radical-pair pathway.[9d]

Conclusion

Some 4-substituted benzyl sulfoxylates **7** were prepared and isolated. The yields are optimized through low-temperature control during the reaction. The isomerization process of **7b**,**c** to the corresponding sulfinates **8b**,**c** follows first-order kinetics, in C_7D_8, $CDCl_3$, and CD_3CN, and is likely achieved via a three-membered ring activated complex in the transition state where the sulfur from the O−S−O functionality acts as an electron donor on the adjacent benzylic carbon. The solvent polarity has little effect on the rate constant and can be interpreted in terms of solvation of the *para* substitutent on the benzene ring of **7b** instead of solvation of the activated complex. The inductive effects for **7b**,**c** as well as the resonance effect for **7b** transmitted through the aromatic ring are believed to be responsible for their stability compared to **7a**,**d**,**e**. The nature of the *para* substituent is probably very important in the overall stability of sulfoxylates **7** and the mechanism of the isomerization process.

(8) Fieser, M.; Fieser, L. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, p 1122.

(9) (a) Braverman, S. *Reactions Involving Sulfenic Acids and Their Derivatives*; Patai S., Ed.; John Wiley & Sons: Toronto, 1990; Chapter 8. (b) Braverman, S.; Sredni, B. *Tetrahedron* **1974**, *30*, 2379. (c) Miller, E. G.; Rayner, D. R.; Thomas, H. J.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4861. (d) Gregory, D. D.; Jenks, W. S. *J. Org. Chem.* **1998**, *63*, 3859.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were recorded at 200 and 300 MHz in the deuterated solvents indicated. Low-resolution electron impact (EI) and chemical ionization (CI) mass spectra were obtained using a 70 eV ionizing energy source and used in direct-inlet mode. Chemical reagents were obtained from Aldrich Chemical Co. and the purity was always verified. Sulfur dichloride, SCl_2, was distilled twice from 0.1% phosphorus pentachloride, PCl_5, and the red fraction boiling from 58 to 60 °C was collected and stored in the freezer under N_2.[8] Column chromatography was carried out on Merck Kieselgel 60 (230−400 mesh). The X-ray structure of **7b** has been deposited at the Cambridge Crystallographic Data Center.

Dibenzyl Sulfoxylate 7a. To a solution of benzyl alcohol (1.0 g, 9.3 mmol) and Et_3N (1.4 mL, 9.3 mmol) in CH_2Cl_2 (25 mL) cooled at −78 °C was added dropwise a solution of SCl_2 (314 μL, 4.65 mmol) in CH_2Cl_2 (4 mL), and the resulting mixture was stirred for 2 h at −40 °C. The mixture was allowed to reach 0 °C, transferred to a separatory funnel, and washed with water (3 × 10 mL), and dried over anhydrous $MgSO_4$, and the solvent evaporated under reduced pressure. Column chromatography of the crude mixture (hexanes−CH_2Cl_2−toluene in 2:1:1) gave **9a** as an off-white solid: mp (hexanes−*t*-BuOH) 50−51 °C (lit.[2] 58−59 °C); (276 mg, 22%); R_f 0.49; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.70, 4.90 (ABq, J = 11.67 Hz, 2H), 7.34 (s, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 76.74 (CH_2), 128.48, 128.53, 128.65, 136.54 (Ar); MS (EI, direct inlet, 1.6 V) *m*/*z* 278 ($M^{\bullet+}$, 38), 230 ($M^{\bullet+}$ − S=O, 100), 180 ($M^{\bullet+}$ − $H_2S_2O_2$, 33), 105 ($C_6H_5^-(CH_2)_2^+$, 30), 91 (C_6H_5-CH_2^+, 100), 77 (Ph^+, 14); **7a** (305 mg, 27%) R_f 0.44; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.11 (s, 2H), 7.39 (s, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 81.86 (CH_2), 128.44, 128.48, 128.61, 136.92 (Ar); **10a** as a clear colorless oil (195 mg, 16%) R_f 0.15; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.93, 5.05 (ABq, J = 11.75 Hz, 2H), 7.36 (s, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 64.07 (CH_2), 128.49, 128.59, 128.64, 135.04 (Ar); MS (CI, direct inlet, 100 °C) *m*/*z* 280 (M + NH_4^+, 100), 216 (M + NH_4^+ − SO_2, 40).

Bis(4-nitrobenzyl) Sulfoxylate 7b. According to the procedure described for **7a**, starting with 4-nitrobenzyl alcohol (1.0 g, 6.5 mmol), Et_3N (910 μL, 6.53 mmol), and SCl_2 (207 μL, 3.27 mmol) in CH_2Cl_2 (3 mL), we obtained a crude that was taken up in CH_2Cl_2 until almost completed dissolution and filtered once more. The filtered solution was left overnight at −30 °C under N_2. Light orange crystals were collected to give **7b** (530 mg, 50%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.17 (s, 2H), 7.46 (d, J = 8.79 Hz, 2H), 8.18 (d, J = 8.54 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 80.33 (CH_2), 123.71, 128.50, 143.73, 147.91 (Ar); the corresponding sulfinate **8b** ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.18 (d, J = 1.46 Hz, 2H), 5.08, 5.13 (ABq, J = 13.13 Hz, 2H), 7.38−7.53 (m, Ar H, 4H) 8.16−8.31 (m, Ar H, 4H); ^{13}C NMR (74.5 MHz, $CDCl_3$) δ 63.25, 68.89, 123.72, 123.82, 128.51, 131.59, 135.34, 143.73, 147.76, 147.91; the remaining was chromatographed (20% CH_2Cl_2 in hexanes) to give **9b** as a off-white powder, mp 95−97 °C (acetone−hexanes) (179 mg, 15%); ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.88, 4.99 (ABq, J = 12.18 Hz, 2H), 7.48 (d, J = 8.82 Hz, 2H) 8.20 (d, J = 8.71 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 75.05 (CH_2), 123.70, 128.61, 143.55, 147.77 (Ar); MS (EI, direct inlet, 423 mV) *m*/*z* 320 ($M^{\bullet+}$ − S=O, 8), ($M^{\bullet+}$ − SO_2, 15), 151 (HONO-C_6H_4-C=O^+, 47), 136 (O_2N-C_6H_4-CH_2^+, 100), 106 (136^+ − NO, 35), 89 (136^+ − HONO, 27), 77 (Ph^+, 63). Anal. Calcd for $C_{14}H_{12}O_6N_2S_2$: C, 45.62; H, 3.28; N, 7.61. Found: C, 45.53; H, 3.07; N, 7.23. R_f: 0.67. **10b** as a yellow solid, mp 81−82 °C (180 mg, 16%); R_f 0.27; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.03, 5.17 (ABq, J = 12.40 Hz, 2H), 7.50 (d, J = 8.50 Hz, 2H) 8.21 (d, J = 8.50 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 62.93 (CH_2), 124.27, 128.91, 142.34, 148.32 (Ar); MS (CI, direct inlet, 300 °C) *m*/*z* 354 (M + NH_4^+, 4), 272 ($M^{\bullet+}$ − SO_2, 6); MS (EI, direct inlet, 3.9 V) *m*/*z* 353 (M − $H^{\bullet+}$, 1). Anal. Calcd for $C_{14}H_{12}O_7N_2S$: C, 47.71; H, 3.43; N, 7.96. Found: C, 47.71; H, 3.23; N, 7.81.

Bis(4-chlorobenzyl) Sulfoxylate 7c. Starting with 4-chlorobenzyl alcohol (1.0 g, 7.0 mmol), Et_3N (978 μL, 7.02 mmol), and SCl_2 (238 μL, 3.50 mmol) in CH_2Cl_2 (3 mL), we obtained a crude that was chromatographed (60% CH_2Cl_2 in hexanes)

very quickly to give fractions as mixture of **9c** and **7c**: R_f 0.68; the sulfite **10c** (195 mg, 17%). The mixed fractions were chromatographed in hexanes−CH_2Cl_2−toluene (2:1:1) very quickly to give **9c** as clear shiny pellets, mp (pentane) 46−48 °C (204 mg, 17%): R_f 0.60; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.76, 4.86 (ABq, J = 10.41 Hz, 2H) 7.24−7.36 (m, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 75.76 (CH_2), 128.72, 129.91, 134.40, 134.93 (Ar); the sulfoxylate **7c** (500 mg, 46%) R_f 0.56; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.00 (s, 2H), 7.28 (d, J = 10.28 Hz, 2H), 7.32 (d, J = 7.21 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 81.05 (CH_2), 128.71, 129.81, 129.91, 135.34 (Ar).

Bis(4-methoxybenzyl) Sulfoxylate 7d. Starting with 4-methoxybenzyl alcohol (1.0 g, 7.2 mmol), Et_3N (1.0 mL, 7.2 mmol), and SCl_2 (246 μL, 3.60 mmol), we obtained the results reported in Table 1.

Bis(4-methylbenzyl) Sulfoxylate 7e. Starting with 4-methylbenzyl alcohol (1.0 g, 8.2 mmol), triethylamine (1.14 mL, 8.18 mmol), and SCl_2 (278 μL, 4.10 mmol) in CH_2Cl_2 (3 mL), we obtained a semisolid residue that was chromatographed (50% CH_2Cl_2 in hexanes) to give the dialkoxy disulfide **9e** as an off-white clear liquid (225 mg, 18%): R_f 0.55; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.38 (s, 3H), 4.80, 4.90 (ABq, J = 10.78 Hz, 2H), 7.20 (d, J = 7.86 Hz, 2H), 7.28 (d, J = 7.93 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 21.23, 76.59 (CH_2), 128.77, 129.18, 133.55, 138.31 (Ar); MS (EI, direct inlet, 150 °C) m/z 258 ($M^{\bullet+}$ − S=O, 0.1), 242 ($M^{\bullet+}$ − SO_2, 0.2), 210 ($M^{\bullet+}$ − $H_2S_2O_2$, 0.5), 105 (CH_3-C_6H_4-CH_2^+, 100), 91 (C_6H_4-CH_2^+, 36), 77 (Ph^+, 16); the sulfoxylate **7e** (236 mg, 21%) R_f 0.47; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.40 (s, 3H), 5.12 (s, 2H), 7.25−7.32 (br, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 21.58, 77.30 (CH_2), 129.34, 129.70, 134.28, 139.04 (Ar); the sulfite **10e** as a light yellow solid (20% EtOAc in hexanes), mp 40−42 °C (273 mg, 23%) R_f 0.20; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.32 (s, 3H), 4.84, 4.96 (ABq, J = 11.53 Hz, 2H), 7.11−7.22 (m, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 21.22, 64.06 (CH_2), 128.67, 129.32, 132.02, 138.53 (Ar); MS (EI, direct inlet, 30 °C) m/z: 290 ($M^{\bullet+}$, 1), 226 ($M^{\bullet+}$ − SO_2, 0.1), 105 (CH_3−C_6H_4−$CH_2^{\bullet+}$, 100); the corresponding sulfinate **8e** (oil, 79 mg, 7%) R_f 0.04; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.93, 4.02 (ABq, J = 13.18 Hz, 2H), 4.89, 4.99 (ABq, J = 11.48 Hz, 2H), 7.12, 7.13 (two singlets, 8H); ^{13}C NMR (74.5 MHz, $CDCl_3$) δ 21.18, 21.23, 64.10, 70.31, 125.64, 128.43, 129.25, 129.46, 130.36, 132.64, 138.08, 138.46.

Isomerization of Bis(4-chlorobenzyl) Sulfoxylate 7c to the Sulfinate 8c. The isomerization to the sulfinate was observed: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.98, 4.02 (ABq, J = 12.94 Hz, 2H), 4.90, 5.01 (ABq, J = 11.96 Hz, 2H), 7.11−7.38 (m, H Ar, 8H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 63.54, 69.71, 128.70, 128.82, 128.96, 129.62, 129.80, 131.79, 133.95, 134.54; MS (EI, direct inlet, 30 °C) m/z 266/268 ($M^{\bullet+}$ Cl cluster 0.15/0.15), 142/144 (4-Cl-C_6H_4-$CH_2OH^{\bullet+}$ Cl cluster, 83/27), 107 ($142^{\bullet+}$ − Cl, 100), 77 (Ph^+, 96).

X-ray Crystallographic Analysis of 7b. Pure colorless crystals were obtained from CH_2Cl_2. The principal crystallographic parameters of compound **7b** are as follows: M = 336.32; triclinic; space group $P1$; a = 7.728(2) Å, b = 8.011(2) Å, c = 12.553 Å; α = 89.13(2)°, β = 79.74(2)°, γ = 73.73(2)°; V = 733.6(3) Å^3; Z = 2; D_c = 1.523 g/cm^3; Mo Kα; λ = 0.70930 Å; μ = 0.255 mm^{-1}; F(000) = 348. The structure was refined to a final R = 0.0704, R_w = 0.1132 for 2588 reflections, $I > 2\sigma(I)$.

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Supporting Information Available: An ORTEP presentation for **7b**. Time dependence isomerization of **7c** to **8c** in $CDCl_3$ at 20.5 °C. Detailed ^{1}H NMR and ^{13}C NMR data (**7a**−**c**,**e**; **8b**,**e**; **10a**−**c**,**e**) and MS data for **10a**,**e**. Note that analytical data including ^{1}H NMR and ^{13}C NMR for **9a**−**e** and MS for **9a**,**b** were previously submitted as Supporting Information (ref 4b). This material is available free of charge via the Internet at http://pubs.acs.org.

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