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This paper is dedicated to Professor Juzo Nakayama on the occasion of his 65th birthday and retirement.

Lithium alkanethiolates do not react with *N*-sulfonyloxaziridine **1** to generate sulfenate species, as uniformly reported in other series. In the present case, a double oxidation reaction is exclusively observed. This unexpected outcome was then exploited for a general, mild and straightforward route to aliphatic sulfinate salts. Investigation of further transformation into sulfones is also described.

Keywords: oxidation; oxaziridine; thiolate; sulfinate; sulfone

1. Introduction

N-Sulfonyloxaziridines are an important class of stable, aprotic and neutral oxidizing reagents, which have found, since pioneering efforts of Davis and coworkers, extensive applications in organic synthesis (*1*). The most relevant developments include the epoxidation of olefins, the enolate-mediated hydroxylation of carbonyl compounds and the oxidation of sulfides to sulfoxides.

A few years ago, an unprecedented oxygen transfer reaction, involving lithium thiolates (R^1SLi) as nucleophiles, was reported by our group (*2*) and allowed an efficient and direct access to the corresponding sulfenate salts (R^1SOLi) (Scheme 1). The unusual oxaziridine **1** derived from pinacolone was identified as the most suitable reagent (*3*). *In situ S*-alkylation with aliphatic halides led to the corresponding sulfoxides in good to excellent yields. The scope of the reaction sequence is broad with successful application to aryl, 1-alkenyl and 1-alkynyl species. To complete this study, the final extension of the aliphatic series was investigated, and the results are presented herein.

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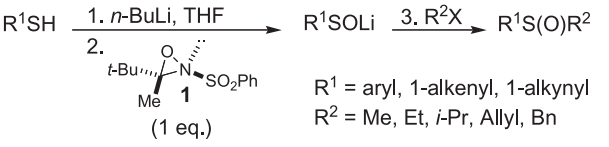


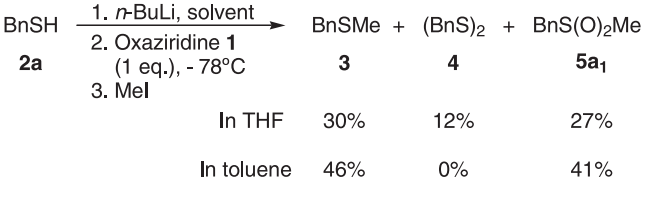
Scheme 1.

2. Results and discussion

A preliminary study with benzyl mercaptan **2a** quickly established that application of the standard protocol (reaction of the lithium thiolate in THF solution with a single equivalent of oxaziridine **1**, followed by trapping experiments with methyl iodide) failed to give the anticipated sulfoxide product, despite instantaneous consumption of the oxidant (Scheme 2). Instead, a mixture consisting of thioether **3**, dibenzyldisulfide **4** and sulfone $\mathbf{5a_1}$ was isolated. These results clearly indicated that mono oxidation leading to sulfenates is not controlled in this case. The reaction furnished instead predominantly the sulfinate salt ($AlkylSO_2Li$), along with minor amounts of disulfide. This striking difference in behavior can probably be ascribed to the enhanced nucleophilicity of the electron-rich aliphatic precursors, in comparison with resonance-stabilized species (*2*) previously tested. Further work in the field indicated that successful conversion into alkanesulfenate requires a much milder oxidant, and the best one identified so far is 2-*t*-butyl-3-phenyloxaziridine (*4*). Switching the solvent from THF to toluene also afforded the double oxidation species but pleasingly led to the disappearance of disulfide side-product (Scheme 2). The sulfone $\mathbf{5a_1}$ and the parent sulfide **3** were produced in equimolecular amounts (41 and 46% isolated yields, respectively).

On the basis of this finding, we decided to study in greater detail the particular reactivity of aliphatic thiolates. We reasoned that by the use of two equivalents of **1**, we might effect complete conversion into sulfinates, thereby providing expeditious access to these species from thiols (*5*) (Scheme 3). Alternative and more conventional routes reported in the literature consist in the treatment of alkyllithium or Grignard reagents with SO_2 or manipulation of sulfonyl chlorides, thiosulfonates, and functionalized sulfones (*6*).

The sequence was repeated employing an excess of the oxidant (2 eq.), and the alkylation was conducted under phase transfer conditions (n-Bu_4NBr) in a toluene/acetone/H_2O system (Condition A), which was particularly efficient in a previous study involving aromatic sulfinates (the intermediate lithium sulfinate failed to react with the electrophile in the initial toluene solution. Successful conversion into the sulfone required readjusting the protocol. See (*5a*)).



Scheme 2.

Scheme 3.

Table 1. Sulfones **5** via sulfinate salts.

Entry	Thiol	Alkyl	R^1	Conditions[a]	Sulfone	Isolated yield (%)
1	**2a**	Bn	Me	A	$\mathbf{5a_1}$	86
2	**2b**	*n*-Bu	Me	A	$\mathbf{5b_1}$	46 (86)[b]
3	**2a**	Bn	Bn	A	$\mathbf{5a_2}$	67
4	**2b**	*n*-Bu	Bn	A	$\mathbf{5b_2}$	49
5	**2a**	Bn[c]	Me	B	$\mathbf{5a_1}$	76
6	**2a**	Bn[c]	Bn	B	$\mathbf{5a_2}$	76
7	**2b**	*n*-Bu	Me	B	$\mathbf{5b_1}$	70
8	**2b**	*n*-Bu	Bn	B	$\mathbf{5b_2}$	67
9	**2c**	2-Furfuryl[c]	Bn	B	**5c**	83
10	**2d**	Cyclohexyl	Bn	B	**5d**	63
11	**2e**	*t*-Bu	Bn	B	**5e**	54[d]

Notes: [a]Condition A: toluene/acetone/H_2O (3:3:4), *n*-Bu_4NBr (cat.), reflux, 24 h, MeI (1.5 eq.) or BnBr (3 eq.); Condition B: DMSO, rt, 18–30 h, MeI (2.5 eq.) or BnBr (1.2 eq.). [b]Isolated yield with 10 eq. of MeI shown in parentheses. [c]Even if this substituent is not a real alkyl group, the carbon bound to the sulfur atom is similarly sp^3-hydridized. [d]The reaction was conducted at 60°C.

We were delighted to isolate the desired sulfone $\mathbf{5a_1}$ in an excellent 86% yield (Table 1, Entry 1). Use of 1-butanethiol likely furnished the corresponding methyl sulfone $\mathbf{5b_1}$ but in a moderate 46% yield (Entry 2). Nethertheless an increase of the electrophile loading up to 10 equivalents led to a significant improvement to 83% yield. Acceptable but somewhat disappointing yields in the range of 49–67% were obtained with benzyl bromide (Entries 3 and 4). These results clearly indicate that the current conditions are not optimized; the efficiency depending both on the sulfinate; structure and the trapping agent nature. Further refinement of this final step is warranted, but the literature offers limited insight, as precedents concern mostly sodium arenesulfinate salts (*7*). Furthermore, a dramatic influence of the counter ion has already been mentioned; the lithiated congeners exhibit generally poor reactivity (*5a*). A survey of the alkylation conditions involving variations of solvent, temperature and the use of additives was then investigated using benzyl thiol **2a** as the model substrate (*8*). The best results were obtained by simply mixing the sulfinate and the electrophilic partner in DMSO at room temperature overnight (conditions B). Sulfones $\mathbf{5a_1}$ and $\mathbf{5a_2}$ were each obtained in 76% yield with methyl iodide and benzyl bromide (Entries 5 and 6).

In order to gain additional information on the alkylation step, we decided to monitor the reaction of benzylic salt **6a** with benzyl bromide (this reaction was chosen as a model example for ease of UV detection because of the presence of chromophors) by micellar electrokinetic capillary chromatography (*9*). This technique is generally able to separate both charged and neutral entities (the four analytes to separate are the sulfinate, the alkyl halide, the sulfone and the DMSO solvent). Analysis of a control sample indicated precipitation of benzyl bromide in the electrophoretic medium, and hence no detection of this species. A nice separation of the remaining components in less than 15 min was achieved by employing a buffer consisting of 30 mM sodium borate and 60 mM sodium dodecyl sulfate, pH 9.3, as shown in Figure 1. Unfortunately, application of these conditions to reaction samples was more problematic. The analysis was probably disturbed by the concomitant liberation of lithium bromide.

With optimized reaction conditions at hand, we proceeded to test the whole sequence on other alkanethiols, incorporating primary, secondary and tertiary structures. In a typical experiment, precursor **2** was deprotonated in THF with *n*-BuLi (1.1 eq.), and the resulting anion was treated at low temperature (−78°C) with *N*-sulfonyloxaziridine **1** (2.1 eq.). Subsequent work-up, including extraction into the aqueous phase (the liberated imine remained dissolved in the organic layer) and concentration, afforded the sulfinate intermediates **6** as pure solids. The mass balance associated with the collected ^{1}H NMR data provides unambiguous evidence for quantitative salt formation

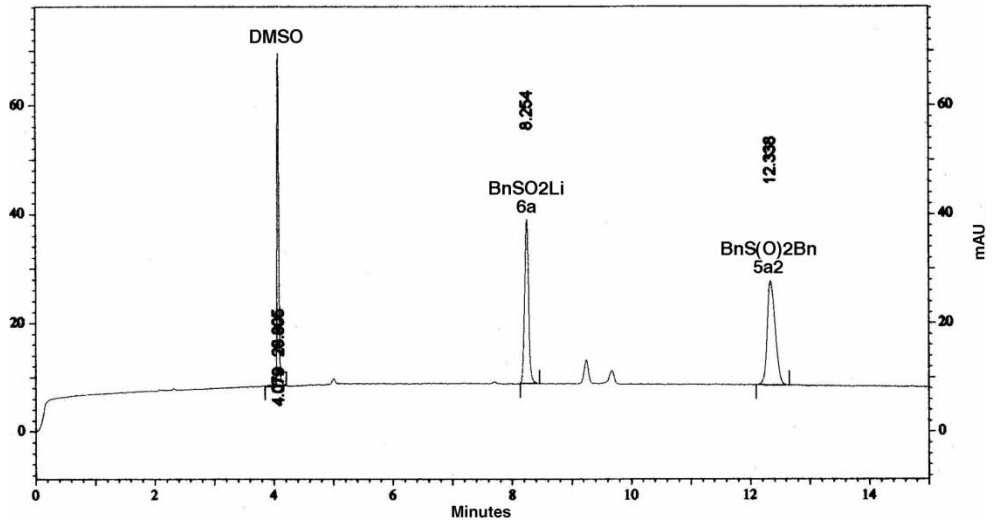


Figure 1. Electropherogram of a control sample prepared with 1.42 mg of **6a**, 0.63 mg of $\mathbf{5a_2}$ and 1 μL of DMSO.

uniformly across the thiol series. Over-oxidation into sulfonate salt ($AlkSO_3^-$) was not detected (*10*), as assessed by reactions carried out with 3 eq. of oxaziridine **1**. The sulfinate was still the sole oxidation product, and unreacted oxidant was fully recovered. Attractive features of this novel oxidation reaction include generality, high efficiency, technical simplicity and the use of extremely mild conditions (−78°C), which might permit a complete chemoselectivity, starting with highly functionalized substrates. The residue was then treated with the electrophile in DMSO to afford sulfones **5**. The results obtained are gathered in Table 1. Worthy of note is that the sulfinate ester, which might arise from the competing *O*-alkylation of the ambident sulfinate, was never detected (*11*).

n-Butyl sulfinate **6b** underwent a clean and efficient transformation under the optimized protocol. Trapping with methyl iodide or benzyl bromide produced sulfones $\mathbf{5b_1}$ and $\mathbf{5b_2}$ in 70 and 67% yields, respectively (Entries 7 and 8). The reaction can also be nicely extended to another primary substrate, providing furfuryl benzyl sulfone **5c** in an 83% yield (Entry 9). Secondary thiolates are also suitable substrates, as highlighted by the formation of the cyclohexyl product **5d** in 63% yield (Entry 10). Finally, a poor result was observed with tertiary sulfinate **6e** (yield below 20%), but raising the temperature to 60°C provided an acceptable 54% yield (Entry 11).

3. Conclusions

To summarize, we described a general and original way to directly convert aliphatic thiols into the corresponding sulfinate salts. The methodology is based on an oxaziridine-mediated oxidation reaction via lithium species. The current protocol shows many benefits in efficiency, ease of purification and functional-group tolerance according to the mild conditions required (rapid reaction at −78°C). Subsequent conversion into sulfones was also investigated, and optimized conditions, in our experience, involve simple treatment with the alkyl halide in DMSO. This work also broadens the scope of synthetic applications of oxaziridines. By a judicious choice of the reagent, we are able to nicely control the oxidation products of thiolates. Use of the poorly reactive 2-*t*-butyl-3-phenyloxaziridine (*4*) led to the sulfenate intermediate, whereas the stronger reagent **1** furnished the sulfinate.

4. Experimental

Dry THF and toluene were dispensed by a PURESOLV™ developed by Innovative Technology Inc. All other reagents and solvents were used as received from commercial sources. Due to the stench of thiols, all glassware and syringes were washed with bleach after use. Melting points were obtained on an Electrothermal IA9000 capillary apparatus and are uncorrected. NMR spectra were obtained on a Bruker DPX 250 spectrometer. IR spectra were recorded on a Perkin Elmer ATR apparatus. Mass spectra were recorded on a Varian GC/MS/MS instrument equipped with CP 3800 (GC) and Saturn 2000 (MS/MS) modules or on a JEOL AX500 instrument equipped with DA5000 and EI70cV modules. Analytic separations by capillary electrophoresis were investigated with a Beckman Coulter P/ACE MDQ system configured with a photo diode array detector and UV source optics. A fused silica capillary (50 cm by 50 μm i.d.) was employed, and the temperature and run voltage were maintained constant at 25°C and 30 kV, respectively. The wavelength of UV detection was set at 214 nm. Oxaziridine **1** was prepared as previously described by us (*2d*). The sole modification concerns the oxidation procedure of the intermediate *N*-sulfonylimine, which was carried out using recently developed conditions with MCPBA/KOH (*12*).

4.1. *General procedure*

To a solution of thiol **2** (1 mmol) in dry toluene (5 ml) cooled to −78°C, *n*-BuLi (769 μL of a 1.43 M solution in hexanes, 1.1 mmol, 1.1 eq) was added dropwise. The mixture was stirred for 15 min, and a solution of oxaziridine **1** (535 mg, 2.1 mmol) in dry toluene (2 ml) was added cautiously dropwise so that the temperature stayed below −70°C. After 30 min at −78°C, the mixture was diluted with EtOAc (10 ml) and extracted with distilled water (3 × 3 ml). The combined aqueous extracts were washed with EtOAc (2 × 20 ml) and then evaporated under reduced pressure to afford the lithium sulfinate salt **6** in quantitative yield. The electrophile [benzyl bromide (1.2 mmol, 1.2 eq.) or methyl iodide (2.5 mmol, 2.5 eq.)] was added to a solution of freshly prepared sulfinate in DMSO (2 ml). The mixture was stirred overnight and then diluted with dichloromethane (25 ml). The organic layer was washed with water (5 × 20 ml), dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude product was then purified by silica gel column chromatography to afford the pure sulfones **5**.

4.2. *Sulfinic acids*

4.2.1. *Phenylmethanesulfinic acid lithium salt (**6a**)*

Prepared from thiol **2a** (Alkyl = Bn). White solid. ^{1}H NMR (250 MHz, D_2O): δ 3.61 (s, 2H), 7.29–7.39 (m, 5H).

4.2.2. *1-Butanesulfinic acid lithium salt (**6b**)*

Prepared from thiol **2b** (Alkyl = *n*-Bu). White solid. ^{1}H NMR (250 MHz, D_2O): δ 0.86 (t, J = 7.7 Hz, 3H), 1.36 (sextet, J = 7.7 Hz, 2H), 1.44–1.53 (m, 2H), 2.33 (t, J = 7.6 Hz, 2H).

4.2.3. *2-Furylmethanesulfinic acid lithium salt (**6c**)*

Prepared from thiol **2c** (Alkyl = 2-furfuryl). Orange solid. ^{1}H NMR (250 MHz, D_2O): δ 3.53 (s, 2H), 6.20–6.23 (m, 1H), 6.29–6.31 (m, 1H), 7.32–7.34 (m, 1H).

4.2.4. *Cyclohexanesulfinic acid lithium salt (**6d**)*

Prepared from thiol **2d** (Alkyl = cyclohexyl). White solid. ^{1}H NMR (250 MHz, D_2O): δ 1.09–2.08 (m, 10H), 2.66–2.76 (m, 1H).

4.2.5. *2-Methyl-2-propanesulfinic acid lithium salt (**6e**)*

Prepared from thiol **2e** (Alkyl = *t*-Bu). White solid. ^{1}H NMR (250 MHz, D_2O): δ 0.93 (s, 9H).

4.3. *Sulfones*

4.3.1. *[(Methylsulfonyl)methyl]benzene (**5a$_1$**)*

Obtained using thiol **2a** (Alkyl = Bn, 1 mmol) and methyl iodide (R^1 = Me) as the electrophile, via sulfinate **6a**. Yield 76% (130 mg, 0.76 mmol). White solid. mp 125–127°C (AcOEt/heptane), lit. (*13*): 125°C (benzene). TLC (AcOEt/heptane, 50:50) $Rf = 0.31$. ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.76 (s, 3H), 4.26 (s, 2H), 7.41 (s like, 5H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 39.1, 61.5, 128.5, 129.3, 130.6. IR (KBr): ν 3012, 2976, 2930, 1496, 1460, 1416, 1302, 1116. MS (CI, MeOH): m/z (%) 171 [$(M + H)^+$, 100], 170 (122), 91 (28), 65 (11).

4.3.2. *(Benzylsulfonylmethyl)benzene (**5a$_2$**)*

Obtained using thiol **2a** (Alkyl = Bn, 1 mmol) and benzyl bromide (R^1 = Bn) as the electrophile, via sulfinate **6a**. Yield 76% (188 mg, 0.76 mmol). White solid. mp 150–151°C, lit. (*14*): 155–157°C. TLC (CH_2Cl_2/heptane, 80:20) $R_f = 0.15$. ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.13 (s, 4H), 7.40 (broad s, 10H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 57.2, 127.6, 128.9 (2C), 129.0, 130.9 (2C). IR (KBr): ν 3164, 3060, 3030, 2936, 1494, 1452, 1422, 1408, 1300, 1114. MS (CI, MeOH): m/z (%) 247 [$(M + H)^+$, 100], 229 (33), 181 (24), 91 (13), 65 (17).

4.3.3. *(1-Methylsulfonyl)butane (**5b$_1$**)*

Obtained using thiol **2b** (Alkyl = *n*-Bu, 1.00 mmol) and methyl iodide (R^1 = Me) as the electrophile, via sulfinate **6b**. Yield 70% (96 mg, 0.70 mmol). White solid. mp 30°C, lit. (*15*): 29–30°C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.98 (t, $J = 7.3$ Hz, 3H), 1.5 (sext, $J = 7.3$ Hz, 2H), 1.80–1.87 (m, 2H), 2.9 (s, 3H), 2.99–3.04 (m, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 13.5, 21.6, 24.4, 40.4, 54.5. IR (KBr): ν 2962, 2874, 1464, 1416, 1292, 1132, 1078. MS (EI): m/z (%) 137 [$(M + H)^+$, 100], 121 (58), 119 (32), 81 (61), 57 (62).

4.3.4. *(Butylsulfonylmethyl)benzene (**5b$_2$**)*

Obtained using thiol **2b** (Alkyl = *n*-Bu, 1.00 mmol) and benzyl bromide (R^1 = Bn) as the electrophile, via sulfinate **6b**. Yield 67% (143 mg, 0.67 mmol). White solid. mp 92–95°C, lit. (*16*): 97–97.5°C. TLC (CH_2Cl_2/pentane, 50:50) $Rf = 0.15$. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.92 (t, $J = 7.25$ Hz, 3H), 1.41 (sext, $J = 7.25$ Hz, 2H), 1.74–1.82 (m, 2H), 2.78–2.85 (m, 2H), 4.22 (s, 2H), 7.40 (s like, 5H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 13.6, 21.8, 23.9, 51.0, 59.6, 128.3, 129.1, 129.2 (2C), 130.6 (2C). IR (KBr): ν 2982, 2952, 2938, 2870, 1496, 1456, 1456, 1404, 1318, 1118. MS (CI, CH_3CN): m/z (%) 213 [$(M + H)^+$, 100], 91 (8).

4.3.5. *2-(Benzylsulfonylmethyl)furan (**5c**) (17)*

Obtained from thiol **2c** (Alkyl = 2-furfuryl, 1.00 mmol) and benzyl bromide (R^1 = Me) as the electrophile, via sulfinate **6c**. Yield 83% (196 mg, 0.83 mmol). Orange solid. mp 84–86°C. TLC (CH_2Cl_2/heptane, 70:30) $Rf = 0.18$. ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.19 and 4.21 (2s, 2H each), 6.46 (dd, J = 1.8 and 3.2 Hz, 1H), 6.54 (d like, J = 3.2 Hz, 1H), 7.38–7.49 (m, 5H) 7.52 (dd, J = 0.8 and 1.8 Hz, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 50.7, 58.4, 111.5, 112.5, 127.6, 129.0 (2C), 129.1, 130.9 (2C), 142.4, 143.9. IR (KBr): ν 2988, 2938, 1494, 1456, 1410, 1304, 1126. MS (EI): m/z (%) 172 [$(M–SO_2)^+$, 18), 91 (23), 81 (100).

4.3.6. *(Benzylsulfonyl)cyclohexane (**5d**)*

Obtained from thiol **2d** (Alkyl = cyclohexyl, 1.00 mmol) and benzyl bromide (R^1 = Me) as the electrophile, via sulfinate **6d**. Yield 63% (151 mg, 0.63 mmol). White solid. mp 102–103 °C, lit. (*18*): 104–105 °C (EtOH). TLC (CH_2Cl_2) $R_f = 0.21$. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.22–2.18 (m, 10H), 2,69–2,76 (m, 1H), 4.20 (s, 2H), 7.40 (s like, 5H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 23.8, 52.8, 60.0, 127.3, 128.7, 131.2. IR (KBr): ν 2932, 2852, 1492, 1452, 1412, 1296, 1124. MS (EI): m/z (%) 239 (MH^+, 9), 91 (100), 65 (22), 55 (40).

4.3.7. *{[(1,1-Dimethylethyl)sulfonyl]methyl}benzene (**5e**)*

Obtained from thiol **2e** (Alkyl = *t*-Bu, 1.00 mmol) and benzylbromide (R^1 = Bn) as the electrophile, via sulfinate **6e**. In this particular case, the alkylation was performed at 60°C. Yield 54% (115 mg, 0.54 mmol). White solid. mp 123–125 °C, lit.(*19*): 123–125 °C. TLC (CH_2Cl_2/heptane, 80:20) $Rf = 0.23$. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.43 (s, 9H), 4.19 (s, 2H), 7.36–7.42 (m, 5H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 25.0, 56.1, 59.1, 127.9, 128.8, 129.0 (2C), 130.6 (2C). IR (KBr): ν 3054, 3032, 2972, 2906, 2876, 1494, 1480, 1458, 1282, 1112. MS (EI): m/z (%) 213 (MH^+, 6), 212 (3), 157 (22), 92 (58), 91 (100), 65 (43), 57 (83), 41 (50).

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