short Vigreux column to give 8.1 g (41%) of **8** as a red liquid: bp 50–57 °C (0.2 mm); IR (neat) 5.97 μm; NMR (CCl_4) δ 1.69 (s, 6), 2.35 (s, 3). GLC (silicone QF-1 on Chromosorb P) showed this sample of **8** to have about 8% of **9** as an impurity.

***S,S*-Dimethyl Dimethyl-3-thioxodithiomalonate (9).** A partially frozen mixture of 14 g (0.3 mol) of methanethiol, 8 g (0.2 mol) of NaOH, and 200 mL of water was stirred vigorously in a Waring blender while a solution of 18.5 g (0.1 mol) of **2** in 100 mL of methylene chloride was added rapidly. A temperature of 10–15 °C was maintained for 15 min by external cooling. The organic phase was separated, dried, and distilled through a short Vigreux column to give 11.9 g (57%) of **9**: bp 81 °C (0.2 mm); n^{20}_D 1.5982; IR (neat) 6.0 μm; UV max (cyclohexane) 215 (log ε 3.76), 311 (3.91); NMR ($CDCl_3$) δ 1.71 (s, 6 H), 2.25 (s, 3 H), 2.60 (s, 3 H).

Anal. Calcd for $C_7H_{12}OS_3$: C, 40.4; H, 5.8; S, 46.2. Found: C, 40.6; H, 5.9; S, 46.0.

1,3,5,5-Tetramethyl-4-thiobarbituric Acid (10). A mixture of 9.25 g (0.05 mol) of **2**, 4.4 g (0.05 mol) of 1,3-dimethylurea, and 30 mL of ethylene dichloride was refluxed for 15 h. Vacuum concentration and recrystallization at low temperatures from small volumes of toluene gave 6.6 g (66%) of **10**: mp 64–65 °C; IR (KBr) 5.82, 6.0 μm; NMR ($CHCl_3$) δ 1.72 (s, 6 H), 3.39 (s, 3 H), 3.82 (s, 3 H).

Anal. Calcd for $C_8H_{12}N_2O_2S$: C, 48.0; H, 6.0; N, 14.0; S, 16.0. Found: C, 48.0; H, 6.3; N, 13.6; S, 15.7.

Poly[1,4-phenylenemethylene-1,4-phenylene(2,2-dimethyl-1-thioxomalonamido)] (11). A mixture of 5.0 g (0.025 mol) of 4,4′-methylenedianiline, 5.3 g of Na_2CO_3, and 60 mL of water was stirred in a Waring blender while 4.63 g (0.025 mol) of **2** in 250 mL of chloroform was added rapidly. The mixture was stirred for 10 min and then poured into an evaporating dish where the chloroform was allowed to evaporate. The resulting polymer was washed with water and dried to give 7.0 g of **11**: softening from 155 to 190 °C; IR (KBr) 6.10, 6.32 μm; {η} (phenol/tetrachloroethane), 0.24.

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Registry No. **1**, 598-26-5; **2**, 29309-53-3; **3**, 78127-90-9; **4**, 78127-91-0; **5**, 78127-92-1; **6**, 78127-93-2; **7**, 29309-62-4; **8**, 78149-15-2; **9**, 78127-94-3; **10**, 78127-95-4; **11** polymer, 78127-54-5; **11** repeating unit, 78198-87-5; thiophosgene, 463-71-8; butylethylketene, 17139-73-0; 2-butyl-3-chloro-2-ethyl-3-thioxopropanoyl chloride, 29309-54-4; cyclopentadiene, 542-92-7; 1,3-dimethylurea, 96-31-1; 4,4′-methylenedianiline, 101-77-9.

Direct Substitution vs. Elimination–Addition in Substitution Reactions of *n*-Butyl 1-Butanesulfinyl Sulfone

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Both aryl α-disulfones (**1**) and sulfinyl sulfones (**2**) are very reactive toward nucleophiles, the reactions taking the course shown in eq 1 and 2, respectively.[1,2] In such reactions the sulfinyl sulfone is the more reactive, generally by a factor of 10^3–10^4.

$$\underset{\mathbf{1}}{ArSO_2SO_2Ar} + Nu^- \rightarrow ArSO_2Nu + ArSO_2^- \quad (1)$$

$$\underset{\mathbf{2}}{ArS(O)SO_2Ar} + Nu^- \rightarrow ArS(O)Nu + ArSO_2^- \quad (2)$$

Recently it was shown[3] that while alkyl α-disulfones, such as *n*-$BuSO_2SO_2Bu$-*n* (**3**), are also reactive toward nucleophiles, their substitution reactions with most nucleophiles proceed via an elimination–addition mechanism (eq 3) rather than by direct substitution at a sulfonyl group (as in eq 1). We were therefore curious whether alkyl

$$\underset{\mathbf{3}}{(n\text{-}PrCH_2SO_2)_2} + Nu^- \xrightarrow[\text{determining}]{\text{rate}} NuH + n\text{-}PrCH{=}SO_2 \xrightarrow{NuH} n\text{-}PrCH_2SO_2Nu + n\text{-}PrCH_2SO_2^- \quad (3)$$

sulfinyl sulfones when reacting with nucleophiles would be found to prefer a reaction pathway involving an initial elimination rather than the direct substitution at the sulfinyl group observed with their aryl counterparts.

A priori one can envisage three different possible courses for initial reaction of a nucleophile with an alkyl sulfinyl sulfone, such as *n*-$BuS(O)SO_2$-Bu-*n*. These are direct substitution at the sulfinyl group (eq 4a), elimination to form a sulfine (eq 4b), and elimination to form a sulfene (eq 4c). Based on the behavior of alkyl α-disulfones,[3] one

$$\underset{\mathbf{4}}{n\text{-}PrCH_2S(O)SCH_2Pr\text{-}n} + Nu^- \xrightarrow{k_{ds}^{SO}} n\text{-}PrCH_2S(O)Nu + n\text{-}PrCH_2SO_2^- \quad (4a)$$

$$\xrightarrow{k_{se}^{SO}} NuH + n\text{-}PrCH{=}S{=}O + n\text{-}PrCH_2SO_2^- \quad (4b)$$

$$\xrightarrow{k_{se}^{SO_2}} n\text{-}PrCH_2SO^- + n\text{-}PrCH{=}SO_2 + NuH \quad (4c)$$

would expect that elimination processes should have the best chance to predominate when the attacking nucleophile is one that is strongly basic, such as an alkoxide ion or a highly basic amine. For this reason we elected to examine first the reactions of (a) CH_3O^- and (b) piperidine with *n*-butyl 1-butanesulfinyl sulfone, *n*-$BuS(O)SO_2Bu$-*n* (**4**), since if these do not show evidence of elimination (eq 4b or 4c) being strongly preferred over direct substitution (eq 4a), it is unlikely that elimination ever competes successfully with direct substitution in reactions of common nucleophiles with alkyl sulfinyl sulfones.

To determine the possible importance of elimination vs. direct substitution in these reactions of **4** we have used two probes: (1) Is the substitution product (*n*-$PrCH_2S(O)OCH_3$ or *n*-$PrCH_2S(O)NC_5H_{10}$) expected for direct substitution formed in significant yield? (2) If it is, is it formed in a deuterated medium with no incorporation of deuterium at the α carbon to the sulfinyl group, or is much or all of the product *n*-PrCHDS(O)Nu, as would be the case if its origin was via addition of NuH to the sulfine (*n*-PrCH=S=O) formed by eq 4b, i.e.

$$n\text{-}PrCH_2S(O)SO_2CH_2Pr\text{-}n \xrightarrow[\text{eq 4b}]{Nu^-} n\text{-}PrCH{=}S{=}O \xrightarrow{NuD} n\text{-}PrCHDS(O)Nu$$

Reaction of sulfinyl sulfone **4** (dissolved in methylene chloride) with a solution of sodium methoxide in methanol led to the formation of methyl 1-butanesulfinate,[4] *n*-

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BuS(O)OMe, in high yield (>70%). When the same reaction was carried out with methanol-*O*-*d*, the sulfinate ester was formed in similar yield with no evidence (as judged from the integrated NMR spectrum) of any significant incorporation of deuterium (<0.05 atom of D) on the carbon adjacent to the sulfinyl group. Reaction of **4** with a 2.5-fold molar excess of piperidine in a 1:1 buffer of this amine and its conjugate acid in dioxane as solvent gave 1-(butylsulfinyl)piperidine, *n*-$BuS(O)NC_5H_{10}$, in yields up to 70%. The identity of this previously unreported sulfinamide was established by its oxidation with *m*-chloroperbenzoic acid to the known[3,5] 1-(butanesulfonyl)piperidine, *n*-$BuSO_2NC_5H_{10}$. When the reaction was carried out with piperidine-*N*-*d*, there was no detectable incorporation of deuterium on the carbon adjacent to the sulfinyl group.

In both the reaction with methoxide and the one with piperidine, the principal product formed is that expected for direct substitution (eq 4a). Furthermore, when these reactions are carried out with either MeOD–MeO^- or $C_5H_{10}ND$–$C_5H_{10}ND_2^+$, the NMR spectra of these products indicate no significant incorporation of deuterium (<0.05 atom D) on the α carbon to the sulfinyl group. This shows that these products are indeed formed by direct substitution and *not* by addition of the elements of the conjugate acid of the nucleophile across the carbon–sulfur double bond of the sulfine *n*-PrCH=S=O. From these results it is clear that with alkyl sulfinyl sulfones, in contrast to alkyl α-disulfones, elimination reactions with nucleophiles (eq 4b or 4c) do not predominate over direct substitution (eq 4a) even when the nucleophiles are ones that are quite strongly basic.

The explanation for the differing behavior of alkyl sulfinyl sulfones and alkyl α-disulfones seems fairly straightforward. As noted earlier, nucleophilic substitution at the sulfinyl group of an aryl sulfinyl sulfone (eq 2) is normally 10^3–10^4 faster than the analogous sustitution at the sulfonyl group of an aryl α-disulfone (eq 1). One would therefore expect that for a given nucleophile direct substitution at the sulfinyl group of alkyl sulfinyl sulfone **4** (eq 4a) would be much faster than the analogous direct substitution at a sulfonyl group in α-disulfone **3**. The mechanism for the elimination in eq 3 has been shown[3] to be $E1cB_i$, with the rate-determining step being removal of a proton adjacent to a sulfonyl group. Given that, and the fact that σ_I for $RCH_2S(O)$ is somewhat smaller than that for RCH_2SO_2,[6] the rate of eq 4c should be smaller than the rate for eq 3. The protons on the α carbon to a sulfoxide are several pK units less acidic than those on the α carbon to a sulfone.[7] This suggests that for a given nucleophile the rate constant for eq 4b will also be significantly smaller than that for eq 3. Collectively these various considerations predict that in reactions with **4** elimination processes (eq 4b and 4c) should be much slower in rate relative to direct substitution (eq 4a) than in the reactions of the same nucleophiles with the corresponding alkyl α-disulfone (**3**), and that one can easily understand why direct substitution (eq 4a) can be the observed reaction pathway with **4** when elimination (eq 3) is the observed pathway for reaction of **3** with the same nucleophile.

Experimental Section

***n*-Butyl 1-Butanesulfinyl Sulfone (4).** To a stirred suspension of sodium 1-butanesulfinate[3] (0.72 g, 5.0 mmol) in 10 mL of anhydrous ether at −5 °C was slowly added a solution of 0.70 g (5.0 mmol) of 1-butanesulfinyl chloride[8] in 10 mL of the same solvent. The mixture was stirred for 1 h and then filtered, and the filtrate was evaporated under reduced pressure at 0 °C. The residue was recrystallized from ether, giving 0.87 g (77%) of **4**: mp 28–30 °C (lit.[9] mp 31 °C); IR ($CHCl_3$) 2980, 2880, 1470, 1408, 1386, 1323 (SO_2), 1126 (SO_2), 1080 (S=O) cm^{-1}; NMR ($CDCl_3$) δ 0.98 (t, 6 H), 1.1–2.2 (m, 8 H), 2.8–3.7 (pair of overlapping m, 4 H).

Reaction of 4 with Sodium Methoxide. A solution of **4** (0.60 g, 2.80 mmol) in an inert solvent (CH_2Cl_2, 10 mL) was rapidly mixed with 5.3 mL of a 0.534 N solution of sodium methoxide in anhydrous methanol. The resulting solution was allowed to stand for 30 min at room temperature. It was then evaporated under reduced pressure to ~10 mL, poured into 150 mL of water, and extracted several times with methylene chloride. The methylene chloride extracts were dried ($MgSO_4$) and then evaporated. Careful chromatography of the residue gave methyl 1-butanesulfinate (0.27 g, 71%) as an oil whose identity was confirmed by spectral comparisons with a known[4] sample: IR (neat) 2970, 2950, 2880, 1470, 1410, 1385, 1125 (s), 990 (s) cm^{-1}; NMR ($CDCl_3$) δ 3.79 (s, 3 H, CH_3O), 2.6–2.9 (m, 2 H, CH_2S=O), 1.2–1.95 (m, 4 H) 0.96 (t, 3 H, CH_3).

Repetition of the reaction with CH_3OD instead of CH_3OH gave the sulfinate ester in essentially the same yield and with an NMR spectrum in which the ratio of the intensity of the signal between δ 2.6 and 2.9 to either that at δ 3.79 or 0.96 was identical within experimental error (±5%) with that obtained in the reaction with CH_3OH.

Reaction of 4 with Piperidine. To 0.46 g (2.06 mmol) of **4** in 10 mL of anhydrous dioxane was rapidly added with good stirring a solution of 0.85 g (10 mmmol) of piperidine and 0.72 g of 70% perchloric acid (5.0 mmol $HClO_4$) in 5 mL of dioxane. After 5 min the reaction mixture was poured into 100 mL of water and extracted 4 times with 25-mL portions of methylene chloride. The CH_2Cl_2 extracts were dried ($MgSO_4$) and evaporated under reduced pressure, and the residue was chromatographed on silica gel. Elution with hexane–ether gave a small amount of material which was not identified. Elution with ether afforded 0.30 g (1.59 mmol, 70%) of an oil identified as 1-(butylsulfinyl)piperidine: IR (neat) 2940, 2860, 1450–1480, 1375, 1300, 1275, 1210, 1150, 1030–1080 (vs), 900 cm^{-1}; NMR ($CDCl_3$) δ 3.16 (m, 4 H), 2.79 (distorted t, 2 H, CH_2S=O), 1.2–1.9 (m, 10 H) 0.96 (t, 3 H); mass spectrum, *m/e* 189 (M^+). For confirmation of its identity, this sulfinamide (0.16 g, 0.85 mmol) was oxidized with 85% *m*-chloroperbenzoic acid (0.17 g) in 20 mL of chloroform. After 3 days at room temperature the reaction mixture was washed 3 times with 5% sodium bicarbonate solution and then with water and dried ($MgSO_4$), and the chloroform was evaporated under reduced pressure. The residue was crystallized from hexane, giving 0.14 g (80%) of 1-(butylsulfonyl)piperidine, mp 38–39.5 °C, identical in all respects with a known[3,5] sample.

The reaction of **4** with piperidine was repeated with piperidine-*N*-*d*[10] and $DClO_4$[3] under otherwise identical conditions. Workup afforded 1-(butylsulfinyl)piperidine in essentially the same yield as before, and the integrated ratio of the triplet at δ 2.79 to that of the triplet at δ 0.96 in the NMR spectrum of this material was, as before, exactly 2:3.

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Registry No. 4, 78186-29-5; sodium 1-butanesulfinate, 16642-95-8; 1-butanesulfinyl chloride, 13455-88-4; methyl 1-butanesulfinate, 673-80-3; piperidine, 110-89-4; 1-(butylsulfinyl)piperidine, 78186-30-8; 1-(butylsulfonyl)piperidine, 2588-51-4.

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