11.66 (br s, 1 H, HON), 3.60–3.54 (m, 1 H, HC(1″)), 2.92–2.76 (m, 2 H, $H_2C(6)$), 2.58–2.47 (m, 1 H, HC(3)), 1.97–1.33 (m, 14 H), 1.26 (d, J = 7.1, 3 H, $H_3C(1')$); ^{13}C NMR (75.5 MHz) δ 162.27 (C(2)), 116.68 (C(1)), 51.32 (C(1″)), 34.68, 33.03, 29.00, 28.09, 25.28, 24.83, 24.30, 24.11, 19.52, 16.28; IR 2938 m, 2858 w, 1593 m, 1479 w, 1450 w, 1381 m, 1360 w, 1317 w, 1215 m, 1182 w, 1145 m, 1118 m, 1072 m; MS (10 eV), m/z 239 (10), 238 (M^+, 48), 221 (14), 208 (14), 203 (11), 192 (23), 157 (36), 111 (100), 110 (28); TLC R_f 0.38 (hexane/EtOAc, 5/3). Anal. Calcd for $C_{13}H_{22}N_2O_2$: C, 65.51; H, 9.31; N, 11.76. Found: C, 65.49; H, 9.29; N, 11.77.

2-(Cyclohexylimino)-3-(2-propenyl)-1-*aci*-nitrocyclohexane (17b): yield 142 mg (60%); mp 96 °C; ^1H NMR (300 MHz) δ 11.54 (br s, 1 H, HON), 5.73–5.67 (m, 1 H, HC(2′)), 5.08–5.03 (m, 2 H, $H_2C(3')$), 3.49–3.46 (m, 1 H, HC(1″)), 2.72–2.65 (m, 2 H, $H_2C(6)$), 2.51–2.39 (m, 1 H, HC(3)), 2.28–2.17 (m, 2 H, $H_2C(1')$), 1.89–1.22 (m, 14 H); ^{13}C NMR (75.5 MHz) δ 160.94 (C(2)), 134.40 (C(2′)), 117.64 (C(3′)), 117.14 (C(1)), 51.55 (C(1″)), 36.83, 34.72, 34.09 (C(3)), 32.89, 25.00, 24.83, 24.30, 24.15, 23.67, 16.01; IR 2938 m, 2857 w, 1593 m, 1450 w, 1379 m, 1358 w, 1226 w, 1211 w, 1190 w, 1145 w, 1120 m, 1072 w; MS (70 eV), m/z 265 (3), 264 (M^+, 16), 219 (15), 218 (70), 204 (28), 137 (27), 136 (100), 122 (13); TLC R_f 0.48 (hexane/EtOAc, 5/3). Anal. Calcd for $C_{15}H_{24}N_2O_2$: C, 68.15; H, 9.15; N, 10.60. Found: C, 68.01; H, 9.22; N, 10.62.

2-(Cyclohexylimino)-3-(1-methylethyl)-1-*aci*-nitrocyclohexane (17c): yield 323 mg (54%); mp 114 °C; ^1H NMR (300 MHz) δ 11.90 (br s, 1 H, HON), 3.57 (m, 1 H, HC(1″)), 2.91–2.80 (m, 1 H, HC(3)), 2.62–2.52 (m, 2 H, $H_2C(6)$), 1.98–1.24 (m, 15 H), 0.99 (2 d, 6 H, $H_3C_a(2')$ and $H_3C_b(2')$); ^{13}C NMR (75.5 MHz) δ 162.80 (C(2)), 117.71 (C(1)), 52.46 (C(1″)), 40.03 (C(3)), 35.04, 32.36, 30.29 (C(1′)), 24.90, 24.30, 24.16, 23.78, 23.22, 20.60 ($C_a(2')$), 19.60 ($C_b(2')$), 16.84; IR 2938 m, 2857 w, 1593 s, 1479 w, 1450 w, 1419 w, 1377 m, 1250 w, 1215 w, 1190 w, 1143 m, 1122 m, 1080 m; MS (10 eV), m/z 267 (8), 266 (M^+, 46), 249 (12), 236 (26), 224 (25), 220 (37), 185 (35), 179 (16), 178 (100), 139 (74), 138 (17), 97 (31), 96 (14); TLC R_f 0.41 (hexane/EtOAc, 5/3). Anal. Calcd for $C_{15}H_{26}N_2O_2$: C, 67.63; H, 9.84; N, 10.52. Found: C, 67.84; H, 10.00; N, 10.49.

2-(Cyclohexylimino)-3-*n*-butyl-1-*aci*-nitrocyclohexane (17d): yield 302 mg (60%); mp 88.5 °C; ^1H NMR (300 MHz) δ 11.70 (br s, 1 H, HON), 3.52–3.46 (m, 1 H, HC(1″)), 2.80–2.52 (m, 3 H, HC(3) and $H_2C(6)$), 1.97–1.26 (m, 20 H), 0.94 (t, J = 6.9, 3 H, $H_3C(4')$); ^{13}C NMR (75.5 MHz) δ 162.29 (C(2)), 116.92 (C(1)), 51.45 (C(1″)), 34.67, 34.27 (C(3)), 32.92, 31.79, 29.16, 25.09, 24.84, 24.35, 24.18, 23.39, 22.21, 16.16, 13.71 (C(4′)); IR 2938 m, 2859 m, 1593 s, 1468 w, 1450 m, 1419 w, 1379 s, 1358 m, 1250 w, 1221 w, 1209 w, 1190 m, 1145 m, 1121 m, 1072 m; MS (10 eV), m/z 281 (4), 280 (M^+, 22), 264 (1), 263 (6), 251 (1), 250 (6), 235 (5), 234 (24), 225 (4), 224 (27), 199 (7), 179 (14), 178 (100), 153 (26), 152 (15), 98 (5), 97 (22), 96 (9); TLC R_f 0.49 (hexane/EtOAc, 5/3). Anal. Calcd for $C_{16}H_{28}N_2O_2$: C, 68.53; H, 10.06; N, 9.99. Found: C, 68.41; H, 10.12; N, 9.97.

2-(1-Methylpropyl)-1-nitrocyclohexene (18): yield 33 mg (10%); ^1H NMR (300 MHz) δ 2.69–2.60 (m, 1 H, HC(1′)), 2.64–2.44 (m, 2 H), 2.18–2.06 (m, 2 H), 1.71–1.58 (m, 4 H, $H_2C(4)$ and $H_2C(5)$), 1.43–1.29 (m, 2 H, $H_2C(2')$), 1.06 (d, J = 5.6, 3 H, $H_3CC(1')$), 0.79 (t, J = 7.4, 3 H, $H_3C(3')$); ^{13}C NMR (75.5 MHz) δ 145.84, 141.50, 36.86 (C(1′)), 27.20, 26.96, 22.84, 22.18, 21.52, 18.39 ($CH_3C(1')$), 12.09 (C(3′)); IR 2965 m, 2936 m, 2867 w, 1539 w, 1520 s, 1457 w, 1452 w, 1440 w, 1362 w, 1350 w, 1120 w, 1091 w; TLC R_f 0.65 (hexane/EtOAc, 5/3).

Reduction–Elimination. General Procedure. To a magnetically stirred solution of the nitro imine (17) in ethanol (15 mL/mmol of 17) was added $CeCl_3 \cdot 7H_2O$ (2 mmol/mmol of 17) in one portion. Sodium borohydride (2 mmol/mmol of 17) was then added in small portions at room temperature, and the foamy mixture was stirred for 4 h. Nitro imines **17a** and **17c** were heated to 50 °C for 2 h and 12 h, respectively. After the indicated times, the reaction mixtures became white and milky and were quenched by the addition of acetone (4 mL/mmol of 17) and water (8 mL/mmol of 17). The milky solution was poured into water (40 mL/mmol of 17), and the aqueous solution was extracted with hexane (3 × 50 mL/mmol). The emulsions were dissolved with 10% acetic acid, and washed with half-saturated sodium bicarbonate solution, water, and brine (each 50 mL/mmol of 17). The aqueous washes were back-extracted with hexane (50 mL/mmol of 17), dried over sodium sulfate, filtered, and concentrated. Column chromatography (EtOAc/hexane, 1/15) afforded the desired nitroalkenes **10a–d**, which were shown to be identical with those obtained in the hydrazone sequence (^1H NMR, IR, GC purity >98%). The spectroscopic data from **10** was consistent with data reported in the literature.[4g]

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Registry No. **1**, 112683-19-9; **2**, 112683-20-2; **3**, 112683-21-3; **4a**, 112683-22-4; **4b**, 112683-23-5; **4c**, 112683-24-6; **4d**, 112683-25-7; **4e**, 112683-26-8; **5a**, 112683-27-9; **6a**, 112683-28-0; **7**, 112683-30-4; **7a**, 112683-31-5; **7b**, 112683-32-6; **7c**, 112683-33-7; **7d**, 112683-34-8; **7e**, 112683-35-9; **7e′**, 112790-19-9; **8a**, 112683-36-0; **9a**, 112683-37-1; **10**, 2562-37-0; **10a**, 68216-48-8; **10b**, 112683-38-2; **10c**, 112683-39-3; **10d**, 112683-40-6; **10e**, 112683-41-7; **11a**, 112683-42-8; **12a**, 112683-43-9; **16**, 112683-44-0; **17a**, 112683-45-1; **17b**, 112683-46-2; **17c**, 112683-47-3; **17d**, 112683-48-4; **18**, 112683-49-5; **19**, 112683-50-8; $CH_2{=}CHCH_2I$, 556-56-9; $(CH_3)_2CHI$, 75-30-9; $CH_3(CH_2)_3I$, 542-69-8; (*E*)-$CH_3CH{=}CH(CH_2)_3I$, 112683-29-1; 2-nitrocyclohexanone, 4883-67-4; 1-acetoxycyclopentene, 933-06-2; 2-nitrocycloheptanone, 13154-27-3; 2-nitrocyclopentanone, 22498-31-3; cyclohexylamine, 108-91-8.

Peroxidation of *S*-(2-Methyl-2-propyl) 2-Methyl-2-propanesulfinothioate

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Oxidation of 1 equiv of *S*-(2-methyl-2-propyl) 2-methyl-2-propanesulfinothioate (1) with 2 equiv of *m*-chloroperoxybenzoic acid (MCPBA) gives *S*-(2-methyl-2-propyl) 2-methyl-2-propanesulfonothioate (**4**, 13%), 2-methyl-2-propanesulfenic 2-methyl-2-propanesulfonic thioanhydride (**5**, 32%), 2-methyl-2-propyl 3-chlorobenzoate (**11**, 4%), 2-methyl-2-propyl 2-methyl-2-propanesulfinate (**12**, 22%), and small amounts of bis(2-methyl-2-propyl) trisulfide (**7**) and bis(2-methyl-2-propyl) tetrasulfide (**10**). Possible mechanisms for product formation are discussed.

Introduction

Although it is generally accepted that sulfinothioic acid *S*-esters, (thiosulfinates) are peroxidized to sulfonothioic acid *S*-esters (thiosulfonates), the peracid oxidation of *S*-(2-methyl-2-propyl) 2-methyl-2-propanesulfinothioate (1) may follow a different course. Freeman and Angeletakis[1,2] observed that the low-temperature *m*-chloroperoxybenzoic acid (MCPBA) oxidation of 1 led to diastereomeric *vic*-disulfoxides (α-disulfoxides, **2**, **3**).[1-5] Asakawa

(1) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1981**, *103*, 6232.
(2) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1983**, *105*, 4039.

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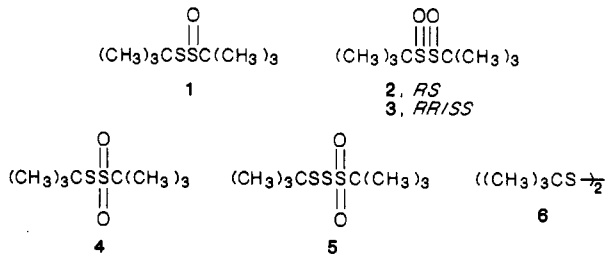
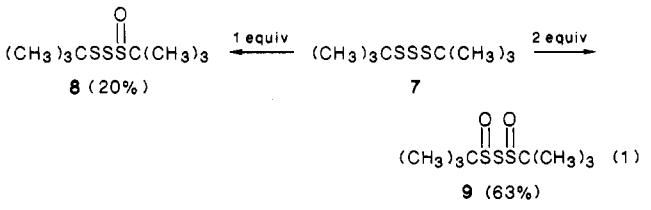
and co-workers[6] reported that 1 was oxidized by peracetic acid to *S*-(2-methyl-2-propyl) 2-methyl-2-propanesulfonothioate (4). Subsequently, Kice and co-workers[7] obtained a mixture of 4[6,8] and 2-methyl-2-propanesulfenic 2-methyl-2-propanesulfonic thioanhydride (5),[9-11] with the latter strongly predominating, from the peracetic acid oxidation of 1. Bass and Evans[10] reported thioanhydride 5 as the only isolated product from the peracetic acid oxidation of commercial bis(2-methyl-2-propyl) disulfide (6)[12] in the presence of anhydrous tungsten(VI) oxide.[13-17]



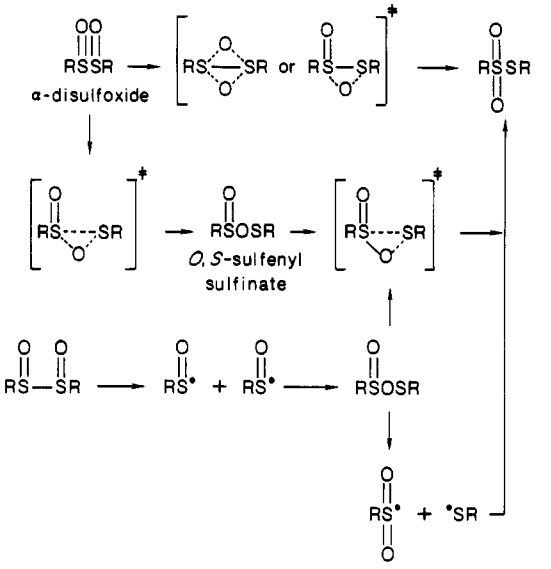
An investigation was undertaken to ascertain whether thioanhydride 5 arose from thiosulfinate 1, α-disulfoxides (2, 3),[1-5] thiosulfonate 4, or bis(2-methyl-2-propyl) trisulfide (7, eq 1)[14,18-20] and to determine the products from the 1-equiv and 2-equiv MCPBA oxidation of thiosulfinate 1.

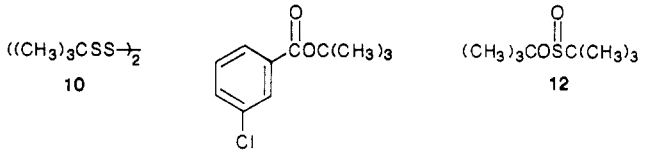


Results

S-(2-Methyl-2-propyl) 2-methyl-2-propanesulfinothioate (1)[7,14,15] was prepared (93% yield) by the MCPBA oxidation of bis(2-methyl-2-propyl) disulfide (6).[7,21,22] In addition to thiosulfinate 1, trisulfide 7, bis(2-methyl-2-propyl) tetrasulfide (10, 1%),[23-25] small amounts of thiosulfonate 4, small amounts of thioanhydride 5, and 2-methyl-2-propyl 3-chlorobenzoate (11) were obtained.

Scheme I





Treatment of 1 equiv of thiosulfinate 1 with 1 equiv of MCPBA in dichloromethane for 48 h at 22–24 °C (72% conversion) led to a 3:1 ratio of thioanhydride 5 to thiosulfonate 4 and small amounts of polysulfides 7 and 10. Treatment of 1 equiv of thiosulfinate 1 with 1 equiv of MCPBA in dichloromethane for 3 h at 22–24 °C followed by reflux for 2 h (73% conversion) afforded a small amount of polysulfides 7 and 10, thiosulfonate 4 (24%), and thioanhydride 5 (76%). Thiosulfinate 1 is stable in the presence of 3-chlorobenzoic acid (MCBA) in dichloromethane under these experimental conditions.

One equivalent of thiosulfinate 1 was peroxidized with 2 equiv of MCPBA in dichloromethane at 0–24 °C (30 min) and at 22–24 °C (10 h; 98.8% conversion). In addition to small amounts of polysulfides 7 and 10, thiosulfonate 4 (13%), thioanhydride 5 (32%), ester 11 (4%), and 2-methyl-2-propyl 2-methyl-2-propanesulfinate (12, 22%) were isolated.

Thiosulfonate 4 shows ^{1}H NMR resonances at δ_H 1.46 and 1.61 and ^{13}C NMR resonances at δ_C 23.73, 31.53, 56.39, and 68.09.[1,10] Thioanhydride 5 has ^{1}H NMR resonances at δ_H 1.41 and 1.49[7,9,10] ^{13}C NMR resonances for 5 were observed at 24.29, 29.92, 49.97, and 70.12.[7]

2-Methyl-2-propyl 3-chlorobenzoate (11), shows the *tert*-butyl ^{1}H NMR signals at δ 1.59 and aromatic resonances from δ 7.32 to 7.88.[26] 2-Methyl-2-propyl 3-

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(10) Bass, S. W.; Evans, S. A., Jr. *J. Org. Chem.* **1980**, *45*, 710.
(11) Block and O'Connor[9] reported that thioanhydride 5 results from the thermal degradation (7%, 96 °C for 8 h) of thiosulfinate 1.
(12) Technical grade (Aldrich) bis(2-methyl-2-propyl) disulfide (6) contained 15% bis(2-methyl-2-propyl) trisulfide (7).
(13) Kice and co-workers[14] observed 2-methyl-2-propanesulfenic benzenesulfonic thioanhydride ($PhSO_2SSBu$-*t*) during the sulfide-catalyzed decomposition of *tert*-butyl benzenesulfinothioate (PhS(O)SBu-*t*).
(14) Ju, T.-L.; Kice, J. L.; Venier, C. G. *J. Org. Chem.* **1979**, *44*, 610.
(15) Sulfenic sulfonic thioanhydrides 5[9-11,13-17] have received little study.[17]
(16) (a) Brooker, L. G. S.; Child, R.; Smiles, S. *J. Chem. Soc.* **1927**, 1384. (b) Loudon, J. D.; Livingston, A. *J. Chem Soc.* **1935**, 896. (c) Foss, O. *Acta Chem. Scand.* **1947**, *1*, 307.
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(19) Monoxide 8 disproportionates to thiosulfonate 4, thioanhydride 5, trisulfide 7, and tetrasulfide 10.[20]
(20) Steudel, R.; Latte, J. *Chem. Ber.* **1977**, *110*, 423.
(21) Netscher, T.; Prinzbach, H. *Synthesis* **1987**, 683.
(22) The photosensitized oxidation of bis(2-methyl-2-propyl) disulfide (6) also gives thiosulfinate 1 (75%). Murray, R. W.; Jindal, S. L. *J. Org. Chem.* **1972**, *37*, 3516.
(23) Polysulfides 7 and 10 were an inseparable mixture. Since chemical shifts of protons in RS_nR move downfield in a theoretically predictable way as *n* increases, δ_H at 1.37 was assigned to 7 and δ_H 1.40 was assigned to 10.[24,25] Yields were obtained from integration of the two resonances.
(24) (a) Van Wazer, J. R.; Grant, D. *J. Am. Chem. Soc.* **1964**, *86*, 1450. (b) Grant, D.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1964**, *86*, 3012.
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chloroperoxybenzoate shows the *tert*-butyl ^1H NMR resonance at δ 1.41.[26c]

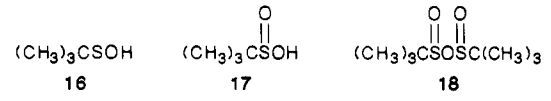
2-Methyl-2-propyl 2-methyl-2-propanesulfinate (12) has ^1H NMR resonances at δ_H 1.16 and 1.43 and ^{13}C NMR resonances δ_C 22.38, 30.24, 57.18, and 82.05. The resonance at δ 57.18 is considered to be associated with the carbon bonded to the sulfinyl sulfur atom and that at δ 82.05 with the carbon bonded to the oxygen atom.[1-3,7,10,27-31]

Discussion

Peroxidation of thiosulfinate 1 takes place at the sulfenyl sulfur atom to afford *vis*-disulfoxides (2, 3). Applying the theory of hard and soft acids and bases (HSAB), the sulfenyl sulfur is expected to be softer than the sulfinyl sulfur. Thus, the more nucleophilic character of the sulfenyl sulfur over sulfinyl sulfur suggests that *vis*-disulfoxides (2, 3) and *O,S*-sulfenyl sulfinates are involved in the formation of thiosulfonate 4 (Scheme I).[1-4,8,27,31-38]

The *O,S*-sulfenyl sulfinate (Scheme I) may rearrange directly to thiosulfonate 4 or dissociate to 2-methyl-2-propanethiyl radical and 2-methyl-2-propanesulfonyl radical, which may recombine to form thiosulfonate 4. However, the absence or small amounts of bis(2-methyl-2-propyl) disulfide (6) and the absence of bis(2-methyl-2-propyl) α-disulfone in the product mixtures mitigate against the latter pathway.[4,5,8,38,39]

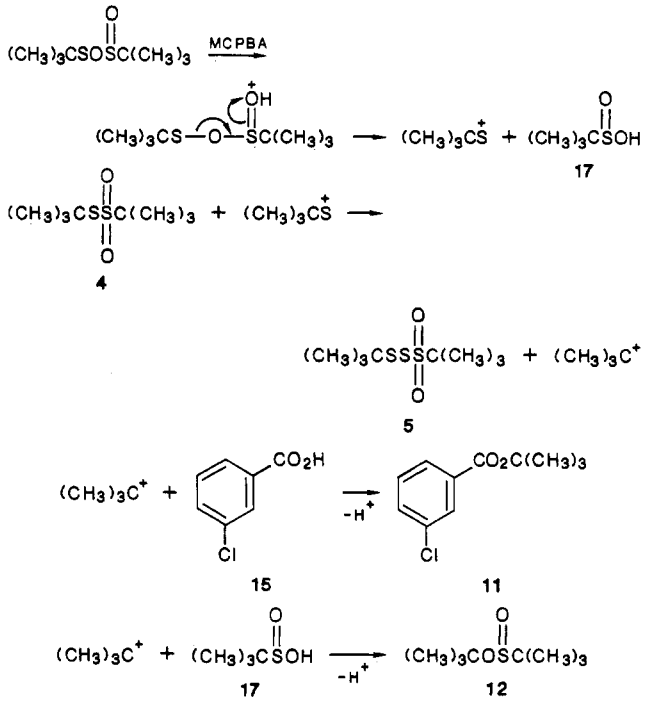
Low-temperature ^1H NMR and ^{13}C NMR studies have shown that 2-methyl-2-propanesulfenic acid (16), 2-methyl-2-propanesulfinic acid (17), and diastereomeric 2-methyl-2-propanesulfinic anhydride (18) are intermediates in the peroxidation of thiosulfinate 1.[1-3] Presumably, MCPBA oxidizes the *O,S*-sulfenyl sulfinate to anhydride 18 which is hydrolyzed to sulfinic acid 17.[40] Hydrolysis of *vic*-disulfoxides (2, 3) or *O,S*-sulfenyl sulfinate leads to sulfenic acid 16 and sulfinic acid 17. Dehydration of sulfenic acid 16[41,42] affords thiosulfinate 1, which can react with sulfenic acid 17 to give thiosulfonate 4.[1-4,43] Dehydration of sulfenic acid 17 to anhydride 18 is another possible source of water as is the reaction of sulfenic acid 16 and sulfinic acid 17 to give thiosulfonate 4.[44]



16 17 18

Another reasonable mechanism that could explain formation of products 4, 5, 11, and 12 could involve acid-catalyzed dissociation of *O,S*-sulfenyl sulfinate to electrophilic *tert*-butyl sulfenium ion [$(CH_3)_3S^+$] and sulfinic acid 17 (Scheme II).[45] Reaction of thiosulfonate 4 and

Scheme II



sulfenium ion leads to thioanhydride 5 and stable *tert*-butyl carbenium ion.[46,47] Formation of ester 11 is reasonable since *tert*-butyl esters are prepared from acids and 2-methylpropene.[26a,b] The formation of sulfinate ester 12 from nucleophilic attack of the sulfinate oxygen atom (hard base) of ambident 2-methyl-2-propanesulfinate anion on the *tert*-butyl carbocation (hard acid)[48] is consistent with the HSAB principle.[49,50] Although sulfinate esters (12) are isomeric with sulfones and may be isomerized (to sulfones) when carbocation formation is favorable,[48] the absence of bis(2-methyl-2-propyl) sulfone in the product mixture may be due to possible steric interference between the bulky *tert*-butyl groups which is absent in ester 12 because of the oxygen bridge.

The stability of thiosulfinate 1 in the presence of 3-chlorobenzoic acid (MCBA) in dichloromethane suggests that it is not the precursor of the *tert*-butyl sulfenium ion or trisulfide 7. Thiosulfonate 4 was also stable under these experimental conditions. The stability of thiosulfinate 1 suggests it is not converted to thioanhydride 5.[9,11] The absence of trisulfide 7 formation from thiosulfinate 1 and thiosulfonate 4 suggests that monoxide 8 may not be the precursor of thiosulfonate 4 and thioanhydride 5.[19,20]

Experimental Section

Melting points were obtained in open capillaries on a Thomas-Hoover melting point apparatus and are uncorrected.

IR spectra were obtained with a Perkin-Elmer 283 spectrophotometer, calibrated with the 1601-cm^{-1} absorption of polystyrene, in CCl_4, as neat films, or as KBr disks.

High-resolution mass spectra were obtained with a VG 7070E-HF mass spectrometer (70 eV). Medium-resolution mass

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spectra were obtained with a Finnigan 9610 GC-EI-CI mass spectrometer with a Nova 3 data system operating at an ionization potential of 70 or 100 eV. Chemical ionization mass spectra were obtained by using 2-methylpropane as the reactant gas.

^{1}H NMR spectra were recorded at 250 MHz (Bruker WM-250), at 300 MHz (GE-Nicolet), and at 500 MHz (GE-Nicolet) with the solvent(s) noted. Chemical shifts (δ) are reported downfield from internal Me_4Si (~0.5% for Fourier transform) at δ 0.00. ^{13}C NMR data were obtained with a Bruker WM-250 or GE-Nicolet 300-MHz spectrometer. The NMR spectra of previously prepared substrates agreed with literature values.

Commercial (Aldrich) $CDCl_3$ was used. Other reagents and solvents were purified by standard procedures. Nitrogen was dried by passing it through a column of Drierite and 5-Å molecular sieves.

Thin layer chromatography was performed on silica gel GF (250-μm thick) glass plates that were developed in a solvent mixture of ethyl ethanoate–hexanes (1:10 by volume). After the solvent had risen to the top, the plates were immersed in phosphomolybdic acid and charred in order to visualize compounds.

Flash Column Chromatography. The product mixtures were placed on a 46 cm × 5 cm diameter column which contained 15 cm of Mallinckrodt silica AR CC-4 100–200-mesh silica gel.[51]

***m*-Chloroperoxybenzoic acid (MCPBA)** of purity of 99+%, by iodometric assay, was prepared by washing the commercial 80–85% material with a phosphate buffer of pH 7.5 and drying the solid at reduced pressure.[52]

***S*-(2-Methyl-2-propyl) 2-Methyl-2-propanesulfinothioate (1).** To a stirred solution of bis(2-methyl-2-propyl) disulfide (**6**, 1.78 g, 10 mmol) in dichloromethane (5 mL) at 0 °C was added dropwise a solution of MCPBA (2.16 g, 11 mmol) in dichloromethane (25 mL) during a 15-min period. The reaction mixture was stirred for 30 min at 0 °C and for 60 min at 22–24 °C. The product mixture was filtered and the filtrate was washed with saturated $NaHCO_3$ (3 × 10 mL) and then with water (10 mL). The organic layer was dried ($MgSO_4$), the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel. Elution with hexanes gave 0.027 g (1.5%) of bis(2-methyl-2-propyl) disulfide (**6** R_f 0.45) and 0.021 g of bis(2-methyl-2-propyl) trisulfide (**7**, R_f 0.5, 1%).[12] Elution with ethyl ethanoate/hexanes (1:10) gave small amounts of thiosulfonate **4** and thioanhydride **5** in a 3:1 ratio and thiosulfinate **1** (90%).

The above reaction was repeated except the ice–water bath was removed after addition of MCPBA. The reaction mixture was stirred for 30 min at 22–24 °C and then refluxed for 1 h. A 93% yield (1.80 g) of thiosulfinate **1** was obtained.

***S*-(2-Methyl-2-propyl) 2-methyl-2-propanesulfinothioate (1):** CIMS, m/z 195 (MH^+), 177, 89; IR (neat) 1175 cm^{-1} (S=O); ^{1}H NMR ($CDCl_3$) δ_H 1.38 (s, 9 H), 1.56 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ_C 24.19, 32.28, 48.56, 59.35 ppm.

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Peroxidation of *S*-(2-Methyl-2-propyl) 2-Methyl-2-propanesulfinothioate (1) with One Equivalent of MCPBA. A solution of MCPBA (1.11 g, 5.5 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of thiosulfinate **1** (1.0 g, 5.15 mmol) in CH_2Cl_2 (5 mL) at 0 °C during a 20-min period. The ice bath was removed, the reaction mixture was stirred at 22–24 °C for 3 h, and the reaction mixture was heated at reflux for 2 h (73% conversion). The product mixture was filtered, and the filtrate was washed with saturated $NaHCO_3$ (3 × 10 mL) and then with water (10 mL). The organic layer was dried over $MgSO_4$ and filtered, the solvent was removed in vaccuo, and the product mixture was separated via flash column chromatography. Elution with hexanes gave a mixture (0.08 g) of tri- (**7**) and tetrasulfides (**10**).[16-18] Elution with ethyl ethanoate/hexanes (1:10) gave thiosulfonate **4** (24%) and thioanhydride **5** (76%).

Peroxidation of *S*-(2-Methyl-2-propyl) 2-Methyl-2-propanesulfinothioate (1) with Two Equivalents of MCPBA. A solution of MCPBA (4.44 g, 26 mmol, 40 mL of dichloromethane) was added dropwise to a solution of thiosulfinate **1** (2.50 g, 13 mmol, 15 mL of dichloromethane) at 0 °C during a period of 30 min. The ice bath was removed, and the reaction mixture was stirred at 22–24 °C for 10 h. The product mixture was filtered, and the filtrate was washed with saturated $NaHCO_3$ (3 × 30 mL) and then with 30-mL portions of water until the washing was neutral (pH 7.0 with pH paper). The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. The product mixture was separated by flash column chromatography. Elution with hexanes gave polysulfides **7** and **10** (0.18 g). Elution with ethyl ethanoate/hexanes (1:10) gave ester **11** (4%) which contained an unidentified impurity, thiosulfonate **4** (13%), and thioanhydride **5** (32%). Elution with ethyl ethanoate/hexanes (1:5) gave sulfinate ester **12** (22%).

2-Methyl-2-propyl 2-methyl-2-propanesulfinate (12): CIMS, m/z 179 (33) (MH^+), 123 (100) 89 (30); IR (neat) 1130 cm^{-1} (S=O); HRMS, calcd 178.1027, obsd 178.1021; ^{13}C NMR δ ($CDCl_3$, central solvent resonance at 77.70 ppm) 22.38, 30.24, 57.18, 82.05.

Relative Stability of *S*-(2-Methyl-2-propyl) 2-Methyl-2-propanesulfinothioate (1). A round-bottomed flask containing 0.10 g (0.51 mmol) of thiosulfinate **1**, 1 mL of dry dichloromethane, and 0.08 g (0.51 mmol) of 3-chlorobenzoic acid (MCBA) was stirred at 22–24 °C for 24 h. TLC analyses showed thiosulfinate **1** and trace amounts of disulfide **6**. Similar results were obtained in the absence of MCBA.

Relative Stability of *S*-(2-Methyl-2-propyl) 2-Methyl-2-propanesulfonothioate (4). A round-bottomed flask containing 0.10 g (0.48 mmol) of thiosulfonate **4**, 1 mL of dichloromethane, and 0.08 g (0.48 mmol) of MCBA was stirred at 22–24 °C for 10 h. TLC analysis showed the presence of thiosulfonate **4** and traces of disulfide **6**.

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