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Formation of Sulfonium Tetrafluoroborates from Reactions of γ,δ-Unsaturated Ketones with Thiols in the Presence of Boron Trifluoride Etherate

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Reaction of 8-methylenepentacyclo[$5.4.0.0^{2,6}.0^{3,10}.0^{5,9}$]undecan-11-one (**2**) with 1,3-propanedithiol and with methanethiol in the presence of $F_3B\cdot OEt_2$ in each case affords mixtures of epimeric cage sulfonium tetrafluoroborates [**5a** + **5b** (81%) and **6a** + **6b** (88%), respectively]. Similarly, 5-hexen-2-one reacts with 1,3-propanedithiol–$F_3B\cdot OEt_2$ to afford a mixture of epimeric sulfonium tetrafluoroborates [**9a** + **9b** (93%)]. Careful fractional recrystallization of this mixture afforded isomerically pure **9a** whose structure was determined by single-crystal X-ray crystallographic analysis. These sulfonium tetrafluoroborate salts readily undergo base-promoted elimination: when refluxed with KOH in aqueous THF, **5a** + **5b** afforded **8** (74%), whereas **6a** + **6b** afforded **7** (73%). In addition, **9a** + **9b** reacted with dry triethylamine in refluxing acetonitrile to afford a mixture of isomeric alkenes, **10** and **11** (78%). We conclude that the reaction of γ,δ-unsaturated ketones with thiols in the presence of boron trifluoride etherate results in the formation of cyclic sulfonium tetrafluoroborate salts with participation of the nonconjugated carbon–carbon double bond in the reaction. The results with 5-hexen-2-one suggest that this reaction may be general in that the carbon–carbon double bond need not be constrained in close proximity to the ketone carbonyl group in order to promote its involvement in this reaction.

In connection with recent studies in our laboratory that involve the synthesis of new alkene-substituted pentacyclo[$5.4.0.0^{2,6}.0^{3,10}.0^{5,9}$]undecanes,[1-3] it became necessary for us to synthesize 8-methylenepentacyclo[$5.4.0.0^{2,6}.0^{3,10}.0^{5,9}$]undecane (**1**). A logical precursor to **1** might be 8-methylenepentacyclo[$5.4.0.0^{2,6}.0^{3,10}.0^{5,9}$]undecan-11-one (**2**) whose synthesis from a readily available starting material, pentacyclo[$5.4.0.0^{2,6}.0^{3,10}.0^{5,9}$]undecane-8,11-dione,[4] has been reported recently.[1] To this end, we initially attempted to prepare a bis(thioketal) of **2** by reacting it with 1,3-propanedithiol in the presence of boron trifluoride etherate. Our plan was to obtain the bis(thioketal) and then to hydrogenolyze the carbon–sulfur bonds with Raney nickel.[5] The formation of bis(thioketals) from the reaction of α,β- or β,γ-unsaturated carbonyl compounds with thioketals in the presence of Brønsted acid or Lewis acid catalysts is a well-established procedure.[6-10] However, instead of the expected bis(thioketal) (**4**), a mixture of epimeric sulfonium tetrafluoroborate salts (**5a** and **5b**) was obtained in 88% yield. The ^{1}H NMR spectrum of the mixture of **5a** and **5b** revealed the absence of vinyl proton absorptions and the presence of two methyl singlets at δ 1.63 and 1.65 (ratio 5:3, see Experimental Section). Additionally, the infrared spectrum of the mixture of **5a** and **5b** displayed strong, broad absorption in the region 998–1132 cm^{-1}, characteristic of tetrafluoroborate salts.[11]

When the reaction with **2** was repeated using methanethiol instead of 1,3-propanedithiol, a mixture of epimeric sulfonium tetrafluoroborate salts (**6a** and **6b**) was obtained in 81% yield. The absence of vinyl proton absorptions in its ^{1}H NMR spectrum and the presence of strong, broad absorption in the region 1012–1130 cm^{-1} in its infrared spectrum are consistent with the structures suggested for **6a** and **6b**.

Both cage sulfonium salts **5** and **6** suffered β-elimination when refluxed with base in THF solution.[12,13] Under these conditions, **6** afforded bis(thioketal) **7** whose structure was established via its Hg(II)-promoted hydrolysis[6,14-16] to the corresponding enone, **2**. However, compound **5** did not behave in analogous fashion to afford **4**. Instead, upon treatment with base, **5** suffered regiospecific β-elimination with concomitant opening of its 1,3-dithiocyclohexane ring, thereby affording the corresponding *S*-allyl derivative, **8**. The syntheses of **5** and **6** from **2** and their respective reactions with base to afford **7** and **8**, respectively are summarized in Scheme I.

We suspected that the unusual involvement of the distant carbon–carbon double bond in the reactions of **2** with 1,3-propanedithiol and with methanethiol might be a consequence of the proximity of the C=O and C=C unsaturation centers in **2**. To obtain further information in this regard, the corresponding reaction of 5-hexen-2-one with 1,3-propanedithiol in the presence of boron trifluoride etherate (methylene chloride solvent) was investigated. Again, a mixture of isomeric sulfonium tetrafluoroborate salts (**9**, 93%) was obtained from this reaction. Separation of epimers was accomplished by careful fractional crystallization (see Experimental Section). The structure of the minor (less soluble) isomer (**9a**) was determined by single crystal X-ray structural analysis.

A perspective view of **9a** is shown in Figure 1. The bond distances, bond angles, and conformational angles are given in Table I. The five- and six-membered rings are cis-fused,

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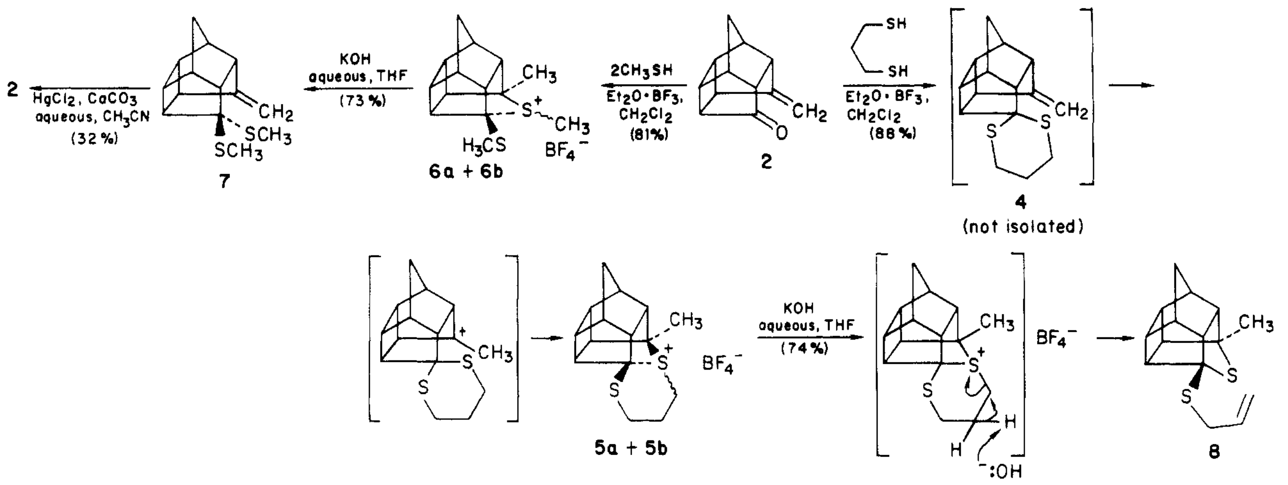
0022-3263/86/1951-0825$01.50/0

Scheme I



with an approximate Cs conformation for the five-membered ring and a chair conformation for the six-membered ring. The two methyl groups C(10) and C(11) are found to be mutually trans. The observed ring system is novel; the most closely related compounds of known molecular geometry that might serve as models for purposes of structural comparison are two 1-thioniabicyclo[4.4.0]decane salts whose structures have been determined by direct methods. In the latter two cases, the bridge S^+–C distance is long, i.e., 1.85 Å[17] and 1.872 Å,[18] when compared to the S(1)–C(6) distance of 1.839 Å that we observe in **9a**. The S(1)–C(9) distance is also long in contrast with the S(1)–C(2) distance in **9a**. This result may be due to strain caused by substitution[19] on C(9). Alternatively, it may be correlated with the small C(9)–S(1)–C(6) bond angle, which indicates that there is increased p character in the hybrid orbitals used for the bonds with C(6) and C(9) that are endocyclic to the five-membered ring in **9a**. Long bond distances would be expected to result from increased p character in these orbitals, with the consequence that the S(1)–C(2) bond (which is exocyclic to the five-membered ring in **9a**) is relatively short. It should be noted, however, that there is a large amount of variation in the observations of both S–C and S^+–C bond distances, and that the nature of this variability is not well understood. The bond angles around S and S^+ in general allow for better structural differentiation (being below 95° for S and above 100° for S^+). However, the normal differences between bond angles around S and S^+ are masked by the strain effects present in the bicyclic system. In particular, we note that the presence of the thioniacyclopentane ring forces C(6)–S(1)–C(9) bond angle to be smaller than normal.

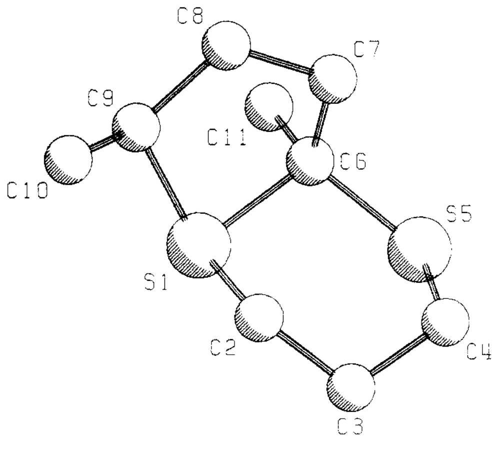
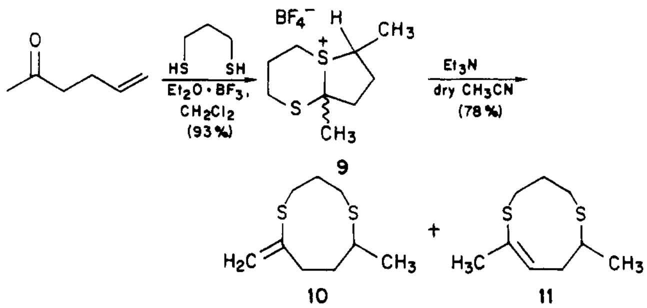


Figure 1. Perspective view of **9a**.

Scheme II



The reaction of **9** with base was also studied. Treatment of **9** (mixture of isomers) with dry triethylamine in dry acetonitrile solvent afforded only two alkenes (**10** and **11**, combined yield 78%), despite the existence of five different pathways for β-elimination in **9** which conceivably could result in the formation of six different alkene products. Separation of the mixture of alkenes **10** and **11** was effected by careful column chromatography (see Experimental Section). The formation of **9** from 5-hexen-2-one and the reaction of **9** with triethylamine to form **10** are summarized in Scheme II.

We conclude from the observations discussed above that, for the examples studied, the reaction of γ,δ-unsaturated ketones with thiols in the presence of boron trifluoride etherate results in the formation of sulfonium tetrafluoroborate salts with participation of the nonconjugated carbon–carbon double bond in the reaction. Furthermore, our results suggest that the corresponding reaction of γ,δ-unsaturated ketones with 1,3-propanedithiol, which results in the formation of cyclic sulfonium salts, may be general in that the carbon–carbon double bond is not required to be spatially constrained (i.e., in close proximity to the ketone carbonyl functionality) in order to promote its involvement in this reaction.

Experimental Section

Melting points and boiling points are uncorrected. ^1H NMR spectra were obtained with a Hitachi Perkin-Elmer Model R-24B NMR spectrometer. ^{13}C NMR spectra were recorded on a JEOL FX-90-Q NMR spectrometer. In all cases, signals are reported

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Table I

Bond Distances, Å	
S(1)–C(2)	1.798 (2)
S(1)–C(6)	1.839 (2)
S(1)–C(9)	1.840 (2)
S(5)–C(4)	1.804 (2)
S(5)–C(6)	1.807 (2)
F(1)–B(1)	1.383 (3)
F(2)–B(1)	1.397 (3)
F(3)–B(1)	1.380 (3)
F(4)–B(1)	1.381 (3)
C(2)–C(3)	1.520 (3)
C(3)–C(4)	1.512 (3)
C(6)–C(7)	1.533 (3)
C(6)–C(11)	1.526 (3)
C(7)–C(8)	1.529 (3)
C(8)–C(9)	1.534 (3)
C(9)–C(10)	1.520 (3)
Bond Angles, deg	
S(1)–C(2)–C(3)	111.2 (1)
S(1)–C(6)–S(5)	108.8 (1)
S(1)–C(6)–C(7)	104.4 (1)
S(1)–C(6)–C(11)	106.7 (1)
S(1)–C(9)–C(8)	107.1 (1)
S(1)–C(9)–C(10)	112.6 (2)
S(5)–C(4)–C(3)	113.7 (1)
S(5)–C(6)–C(7)	117.2 (1)
S(5)–C(6)–C(11)	106.9 (2)
F(1)–B(1)–F(2)	109.3 (2)
F(1)–B(1)–F(3)	109.7 (2)
F(1)–B(1)–F(4)	110.9 (2)
F(2)–B(1)–F(3)	107.5 (2)
F(2)–B(1)–F(4)	109.6 (2)
F(3)–B(1)–F(4)	109.8 (2)
C(2)–S(1)–C(6)	103.5 (1)
C(2)–S(1)–C(9)	103.5 (1)
C(2)–C(3)–C(4)	112.1 (2)
C(4)–S(5)–C(6)	102.2 (1)
C(6)–S(1)–C(9)	92.0 (1)
C(6)–C(7)–C(8)	109.6 (2)
C(7)–C(6)–C(11)	112.4 (2)
C(7)–C(8)–C(9)	111.5 (2)
C(8)–C(9)–C(10)	114.6 (2)
Conformational Angles, deg	
S(1)–C(6)–S(5)–C(4)	−56.5 (1)
C(6)–S(5)–C(4)–C(3)	61.0 (2)
S(5)–C(4)–C(3)–C(2)	−68.6 (2)
C(4)–C(3)–C(2)–S(1)	67.8 (2)
C(3)–C(2)–S(1)–C(6)	−61.2 (2)
C(2)–S(1)–C(6)–S(5)	58.1 (1)
S(1)–C(6)–C(7)–C(8)	−36.8 (2)
C(6)–C(7)–C(8)–C(9)	18.2 (2)
C(7)–C(8)–C(9)–S(1)	9.2 (2)
C(8)–C(9)–S(1)–C(6)	−26.8 (2)
C(9)–S(1)–C(6)–C(7)	36.6 (1)

in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were obtained with a Perkin-Elmer Model 1330 infrared spectrophotometer. Mass spectra were obtained with a Hewlett-Packard Model 5970A GC/MS which was operated at 70 eV. Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and by Midwest Microlab, Indianapolis, IN. Methylene chloride solvent was freshly distilled from phosphorus pentoxide immediately prior to use. Boron trifluoride etherate was distilled immediately prior to use. Acetonitrile was refluxed for 2 h over calcium hydride and then distilled immediately prior to use. Triethylamine was distilled from sodium immediately prior to use. 1,3-Propanedithiol and methanethiol were used as obtained from Aldrich Chemical Co. without additional purification.

Reaction of 2 with 1,3-Propanedithiol. To a flame-dried 250-mL three-necked flask equipped with a thermometer, an addition funnel, an argon inlet–outlet tube, and a magnetic stirring bar was added a solution of **2** (8.6 g, 0.05 mol) in dry methylene chloride (100 mL). This solution was cooled to −4 °C via external application of an ice-salt bath, and boron trifluoride etherate (18.5 mL, 0.15 mol) was added under argon with stirring in such a way that the temperature of the reaction did not exceed −1 °C during the addition. The resulting mixture was stirred for 20 min, at which time a solution of 1,3-propanedithiol (5.4 g, 0.05 mol) in dry methylene chloride (50 mL) was added dropwise during 30 min. After the addition of the dithiol had been completed, the cooling bath was removed, and the reaction mixture was stirred at room temperature (24 h). The reaction mixture then was poured slowly into 5% aqueous sodium bicarbonate solution (300 mL; caution, CO_2 evolved). The resulting mixture was stirred vigorously for 15 min, at which time the layers were separated, and the aqueous layer was extracted with methylene chloride. The combined organic layers were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford **5** as a mixture of epimers **5a** and **5b** (15.41 g, 88%). An analytical sample of **5** was prepared via recrystallization from absolute ethanol, thereby affording a colorless microcrystalline solid, mp 211–212 °C dec (sealed tube). The sample darkened noticeably during heating in the temperature range ca. 190–200 °C: ^{1}H NMR ($CDCl_3$) δ 1.63 and 1.65 (s, ratio 5:3, total 3 H), 1.66 (*A*B, J_{AB} = 11.7 Hz, 1 H), 2.19 (A*B*, J_{AB} = 11.7 Hz, 1 H), 2.47–4.19 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 15.55 (q), 15.55 (q), 23.08 (t), 23.08 (t), 25.57 (t), 25.57 (t), 36.19 (t), 36.95 (t), 39.33 (t), 39.33 (t), 39.33 (d), 39.93 (d), 41.39 (d), 41.77 (d), 44.96 (d), 45.45 (d), 45.61 (d), 45.99 (d), 48.59 (d), 48.81 (d), 49.79 (d), 51.19 (d), 57.80 (d), 58.13 (d), 58.89 (d), 59.92 (d), 78.12 (s), 79.42 (s), 81.37 (s), 82.45 (s); IR (film) 2980 (s), 2915 (m), 2880 (m), 1450 (m), 1428 (s), 1393 (m), 1310 (m), 1285 (s), 1272 (m), 1152 (m), 1138 (s), 1132–998 (br, vs), 975 (m), 901 (m), 840 (m), 730 cm^{-1} (m).

Anal. Calcd for $C_{15}H_{19}BF_4S_2$: C, 51.44; H, 5.47; S, 18.31. Found: C, 51.43; H, 5.74; S, 18.39.

Reaction of 2 with Methanethiol. A 250-mL three-necked flask equipped with a magnetic stirring bar, argon inlet–outlet tube, and rubber septum was flame-dried and then charged with a solution of **2** (10.33 g, 0.060 mol) in dry methylene chloride (120 mL). The solution was cooled by external application of a dry ice–acetone bath. To the cooled solution under argon was added boron trifluoride etherate (23 mL, 0.19 mol) via a syringe. The resulting solution was stirred (15 min) after which time methanethiol (11.04 g, 0.23 mol) was added. The resulting mixture was stirred with application of external cooling (20 min). The inlet–outlet tube was replaced with a rubber septum, and all rubber septa were tightly wired in place. The cooling bath was removed, and the reaction mixture was stirred at room temperature (24 h). Pressure which had built up in the reaction flask during this time was vented via a syringe needle, and the contents of the reaction flask were poured slowly into 5% aqueous sodium bicarbonate solution (350 mL; caution, CO_2 evolved). The resulting mixture was stirred for 20 min, at which time the layers were separated, and the aqueous layer was extracted with methylene chloride. The combined organic layers were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford a mixture of epimers **6a** and **6b** (16.44 g, 81%). An analytical sample of **6** was prepared via recrystallization of this material from absolute ethanol, thereby affording a colorless microcrystalline solid: mp 199–201 °C (sealed tube); ^{1}H NMR ($CDCl_3$) δ 1.63 and 1.66 (s, total 3 H), 1.68 (*A*B, J_{AB} = ca. 11.7 Hz, 1 H), 2.11 (A*B*, J_{AB} = ca. 11.7 Hz, 1 H), 2.26 and 2.31 (s, total 3 H), 2.71 (br s, 3 H), 2.76–3.62 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 13.71 (q), 14.00 (q), 15.03 (q), 15.14 (q), 16.98 (q), 17.41 (q), 38.43 (t), 40.65 (t), 41.08 (d), 41.57 (d), 44.17 (d), 44.39 (d), 44.88 (d), 45.31 (d), 45.42 (d), 48.18 (d), 50.18 (d), 50.67 (d), 53.43 (d), 53.43 (d), 56.74 (d), 56.74 (d), 59.39 (d), 60.04 (d), 78.73 (s), 80.14 (s), 92.06 (s), 92.55 (s); IR (film) 2990 (s), 2882 (m), 1458 (m), 1437 (m), 1393 (m), 1332 (m), 1298 (m), 1289 (m), 1272 (m), 1141 (s), 1130–1012 (br, vs), 1008 (s), 983 (m), 775 (m), 738 cm^{-1} (m).

Anal. Calcd for $C_{14}H_{19}BF_4S_2$: C, 49.71; H, 5.66; S, 18.96. Found: C, 49.79; H, 5.84; S, 19.12.

Reaction of 5a and 5b with Potassium Hydroxide Solution in H_2O–THF. To a suspension of **5a** and **5b** (10.45 g, 0.030 mol) in THF (60 mL) was added a solution of potassium hydroxide (1.68 g, 0.030 mol) in water (5 mL). The resulting mixture was refluxed (1.5 h) and then cooled to room temperature. The reaction mixture was then poured into 5% aqueous sodium bicarbonate solution (300 mL) and stirred (5 min). The resulting mixture was extracted with methylene chloride. The combined organic extracts were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford a yellow oil (6.29 g). This material was purified by column chromatography on silica gel (20% ethyl acetate–hexane eluent); compound **8** (5.84 g, 74%) was thereby obtained as a colorless oil: bp 117–119 °C (0.01 mm); ^{1}H NMR (CDCl$_3$) δ 1.43 (s, 3 H), 1.55 (*A*B, J_{AB} = 11 Hz, 1 H), 1.94 (A*B*, J_{AB} = 11 Hz, 1 H), 2.38–3.08 (m, 8 H), 3.21–3.42 (m, 2 H), 4.95–5.36 (m, 2 H), 5.64–6.15 (m, 1 H); ^{13}C NMR (CDCl$_3$) δ 18.43 (q), 35.05 (t), 40.41 (d), 40.85 (d), 41.71 (t), 44.21 (d), 44.59 (d), 54.12 (d), 54.77 (d), 63.87 (d), 64.25 (d), 68.96 (s), 76.93 (s), 117.02 (t), 134.41 (d); IR (neat) 3078 (w), 2957 (vs), 2862 (s), 1624 (m), 1437 (m), 1278 (m), 1122 (m), 1068 (m), 983 (m), 972 (m), 903 (s), 719 cm^{-1} (m); mass spectrum (70 eV), *m/e* (relative intensity) 264 (4.8), 263 (8.8), 262 (molecular ion, 54.5), 229 (14.7), 221 (33.9), 205 (13.9), 190 (34.2), 189 (100).

Anal. Calcd for $C_{15}H_{18}S_2$: C, 68.65; H, 6.91; S, 24.44. Found: C, 68.55; H, 7.07; S, 24.31.

8,8-Bis(methylthio)-11-methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (7). To a suspension of **6a** and **6b** (6.723 g, 0.020 mol) in THF (50 mL) was added a solution of potassium hydroxide (1.35 g, 0.024 mol) in water (2.0 mL). This mixture was refluxed under argon (45 min) and then cooled to room temperature. The reaction mixture was then poured into a mixture of 5% aqueous sodium bicarbonate solution (250 mL) and ether (50 mL). The resulting mixture was shaken vigorously, and the layers were then separated. The aqueous layer was extracted with ether. The combined ethereal extracts were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford a yellow oil (4.42 g). This crude product was purified via column chromatography on silica gel (pentane eluent); compound **7** was thereby obtained as a colorless oil (3.65 g, 73%): bp 102 °C (0.01 mm); ^{1}H NMR (CDCl$_3$) δ 1.28 (*A*B, J_{AB} = 11 Hz, 1 H), 1.67 (A*B*, J_{AB} = 11 Hz, 1 H), 1.99 (s, 3 H), 2.02 (s, 3 H), 2.11–3.07 (m, 8 H), 4.62 (br s, 2 H); ^{13}C NMR (CDCl$_3$) δ 11.43 (q), 13.54 (q), 34.02 (t), 40.41 (d), 42.20 (d), 43.12 (d), 45.51 (d), 47.13 (d), 47.62 (d), 49.41 (d), 52.71 (d), 68.96 (s), 103.31 (t), 153.10 (s); IR (neat) 3070 (m), 2955 (s), 2920 (s), 2869 (s), 1663 (s), 1440 (s), 1428 (s), 1288 (m), 1280 (m), 1257 (m), 1187 (m), 1091 (m), 964 (m), 875 (s), 826 cm^{-1} (s); mass spectrum (70 eV), *m/e* (relative intensity) 250.1 (molecular ion, 32.8), 204.1 (15.9), 203.1 (100), 156.1 (15.9), 155.1 (60.6), 154.1 (10.6), 153.1 (17.4), 137.0 (55.5), 129.0 (12.1), 128.0 (20.4), 127.1 (11.2), 125.0 (70.9), 124.0 (23.0), 122.0 (17.4), 121.0 (15.7), 115.0 (26.6), 111.0 (62.4), 110.0 (16.5), 109.0 (12.0), 97.0 (10.4), 91.0 (72.6), 89.0 (10.1), 79.0 (40.4), 78.0 (40.8), 77.0 (43.9).

Compound **7** was further characterized via its Hg(II)-promoted hydrolysis to **2**. A 100-mL three-necked flask equipped with an argon inlet-outlet tube, magnetic stirring bar, and glass stoppers was charged with mercuric chloride (1.195 g, 4.4 mmol), calcium carbonate (4.0 g, 0.01 mol), and 80% aqueous acetonitrile solution (30 mL). To the resulting suspension was added dropwise under argon a solution of **7** (0.50 g, 2.0 mmol) in 80% aqueous acetonitrile solution (20 mL) during 20 min. The reaction mixture was stirred vigorously during this period; stirring was continued for 1 h after the addition of **7** had been completed. The reaction mixture was then filtered through a pad of Fuller's earth, and the residue was washed thoroughly with 1:1 methylene chloride–hexane mixed solvent. The filtrate was extracted with 5 M aqueous ammonium acetate solution (5 × 100 mL), and the organic layer was then washed with saturated aqueous ammonium chloride solution (100 mL). The organic layer was then dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford a solid residue. This material was recrystallized from hexane to afford **2** (0.11 g, 32%), mp 71–72 °C (undepressed upon admixture with authentic **2**).

Table II. Crystal Data for 9a

molecular formula	$C_9H_{17}BF_4S_2$
molecular weight	276.2
linear absorption coefficient	3.9 cm^{-1} (Mo Kα)
space group	*Cc*
cell dimensions	
a, Å	8.038 (42)
b, Å	13.013 (21)
c, Å	11.965 (44)
β, degrees	95.23 (62)
volume, Å^3	1246.3
Z	4
density (ρ), g/cm^{-3} (calcd)	1.47
cell determination	24 reflections, Mo Kα_1 (λ = 0.70926 Å)
data collection range	$0 < 2\theta < 60$
radiation	Mo K$\bar{\alpha}$ (λ = 0.71069 Å)
standards	three, remeasured every 200 reflections
temperature of data collection	138 ± 2 K
number of reflections measured	1842
number of reflections observed [$I > 2\sigma(I)$]	1787
final difference Fourier, map max density, e/Å^3	0.3
final *R*	2.61%
R_w	2.82%

Reaction of 5-Hexen-2-one with 1,3-Propanedithiol. A solution of 5-hexen-2-one (24.35 g, 0.248 mol) in dry methylene chloride (500 mL) was cooled to −8 °C via external application of an ice–salt bath. To this cooled solution was added freshly distilled boron trifluoride etherate (95 mL, 0.77 mol) under argon during 10 min. After all of the boron trifluoride etherate had been added, stirring was continued for an additional 10 min, at which time a solution of 1,3-propanedithiol (27.96 g, 0.248 mol) in dry methylene chloride (25 mL) was added to the reaction mixture. The reaction mixture was then stirred under argon and allowed to warm gradually to room temperature. Stirring was continued for 34 h, at which time the solvent was then removed by distillation at atmospheric pressure. The last traces of excess boron trifluoride etherate were removed in vacuo (4 h at 0.01 mm). Absolute ethanol (200 mL) was then added to the oily residue, and this mixture was warmed gently and stirred (15 min), resulting in a homogeneous solution. The solution was cooled overnight in a freezer (−20 °C), during which time **9** (mixture of isomers) crystallized. The crystals were collected by suction filtration, thoroughly washed with hexane, and dried in vacuo; the yield of **9** thereby obtained was 64.0 g (93%). Repeated recrystallization of this material from absolute ethanol afforded an analytical sample of **9** (mixture of isomers) as a colorless microcrystalline solid: mp 148.5–151.5 °C; ^{1}H NMR (CDCl$_3$) δ 1.58 and 1.75 (d, *J* = 7.2 Hz, ratio 1:2, total 3 H), 1.94 (br s, 3 H), 2.0–5.19 (m, 11 H); ^{13}C NMR (CDCl$_3$) δ 13.51 (q), 20.98 (q), 21.15 (q), 21.96 (q), 24.13 (t), 24.40 (t), 26.78 (t), 26.94 (t), 29.76 (t), 33.72 (t), 35.18 (t), 38.43 (t), 38.97 (t), 40.38 (t), 54.63 (d), 61.78 (d), 66.98 (s), 68.93 (s); IR (film, hygroscopic!) 2968 (s), 2894 (m), 1460 (s), 1434 (s), 1397 (s), 1318 (m), 1293 (m), 1460 (s), 1434 (s), 1397 (s), 1318 (m), 1293 (s), 1258 (s), 1198 (m), 1137–1010 (br, vs), 912 (s), 843 (m), 738 cm^{-1} (m).

Anal. Calcd for $C_9H_{17}BF_4S_2$: C, 39.14; H, 6.20; S, 23.22. Found: C, 39.07; H, 6.05; S, 23.48.

Separation of the mixture of **9** isomers was effected via careful fractional recrystallization. A sample of the mixture (ca. 2 g) was dissolved in hot chloroform, and the solution was cooled to room temperature. To this solution was added tetramethylsilane (4–5 drops) and pentane dropwise until turbidity appeared. The resulting mixture was stored overnight in a freezer (−20 °C), during which time crystallization occurred. The crystals were isolated by suction filtration and washed with pentane. A single crystal of isomerically pure **9a** was obtained for X-ray crystallographic analysis via careful recrystallization of this material from acetone–hexane mixed solvent.

Single-Crystal X-ray Structural Analysis of 9a. Preliminary investigations indicated that the crystal system of **9a** is monoclinic. Observations of reflection conditions (*hkl*, *h* + *k* = 2*n*; *h*0*l*, *l* = 2*n*) and further structural calculations confirmed the space group *Cc*. Lattice parameter and intensity data were measured on an Enraf-Nonius CAD-4 automatic diffractometer fitted with a liquid nitrogen low-temperature device. A θ–2θ scan technique was employed using variable scan width and variable scan speed. Maximum scan time for a reflection was 90 s with two-thirds of the time spent on the reflection; the remaining time was divided equally between the high and low backgrounds. The receiving aperture, which had a variable width of (4.0 + 0.86 θ) mm and a constant height of 5 mm, was located 173 mm from the crystal. The intensities of three standard reflections, measured after every 200 reflections, showed no significant variation during the time of data collection, (Table II).

The positions of the two sulfur atoms in **9a** were determined from a Patterson synthesis. The rest of the structure was determined by heavy-atom methods and refined by a full-matrix least-squares routine using anisotropic thermal parameters for the non-hydrogen atoms.[20] All of the hydrogen atoms were located from a difference Fourier map and were refined isotropically. Scattering factors were obtained from "International Tables for X-Ray Crystallography" (Vol. 4, 1974). The refinement converged to a final R $(=\sum||F_o| - F_c||/\sum|F_o|)$ of 0.026 for 1787 observed reflections $[I > 2\sigma(I)]$ and R_w $(=\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ of 0.028. An analysis of the variance after refinement of the data revealed no systematic variation of $\sum w(|F_o| - |F_c|)^2$ with either $\sin\theta$ or F. The final atomic coordinates are listed in Table III. Thermal parameters and hydrogen atomic parameters for **9a** are listed in Tables IV and V, respectively (supplementary material). The atom numbering scheme is given in Figure 1.

Reaction of 9 with Triethylamine. To a solution of **9** (mixture of isomers, 27.42 g, 0.1 mol) in dry acetonitrile (100 mL) under argon was added dry triethylamine (35 mL, 0.25 mol), and the reaction mixture was refluxed under argon (24 h). The reaction mixture was then cooled to room temperature and concentrated in vacuo. The residue was diluted with pentane (200 mL) and stirred vigorously (15 min). The resulting mixture was filtered, and the residue was washed thoroughly with pentane. The filtrate was then concentrated in vacuo to afford a yellow oil (17.61 g). This material was purified by distillation at 58–62 °C (0.02 mm) to afford a mixture of isomeric alkenes **10** and **11** (colorless oil, 14.62 g, 78%). Elemental microanalysis was performed on this mixture of isomers.

Anal. Calcd for $C_9H_{16}S_2$: C, 57.39; H, 8.56; S, 34.05. Found: C, 57.48; H, 8.67; S, 33.95.

Compound **10** was isolated from this mixture in pure form via careful column chromatography on silica gel impregnated with 13% (w/w) silver nitrate (1:3 methylene chloride–pentane eluent). Under these conditions, most of **10** and all of **11** remained on the column after elution: ^{1}H NMR ($CDCl_3$) δ 1.24 (d, J = 7.2 Hz, 3 H), 1.47–2.26 (m, 4 H), 2.35–3.48 (m, 7 H), 5.06 (s, 1 H), 5.24 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.13 (q), 26.44 (t), 27.14 (t), 29.04 (t), 29.63 (t), 33.48 (t), 41.01 (d), 114.58 (t), 145.68 (s); IR (film) 3077 (w), 2917 (s), 1600 (s), 1455 (s), 1379 (m), 1288 (m), 1253 (m), 887 (s), 761 cm^{-1} (m); mass spectrum (70 eV), m/e (relative intensity) 190.1 (M + 2, 3.8), 189.1 (M + 1, 5.4), 188.1 (molecular ion, 39.6), 146.0 (25.7), 127.1 (10.2), 115.0 (13.0), 114.0 (95.3), 113.0 (32.0), 106.0 (40.3), 99.0 (58.1), 85.0 (11.8), 81.1 (24.7), 79.0 (31.9), 77.0 (11.3), 74.0 (11.3), 71.0 (25.0), 65.0 (12.9), 61.0 (12.3), 60.0 (12.8), 59.0 (43.3), 58.0 (37.8), 55.1 (12.2), 53.0 (30.8), 47.0 (35.6), 46.0 (34.3), 45.0 (84.3), 42.0 (11.6), 41.0 (100.0).

The ^{1}H and ^{13}C NMR spectra of **11** can be inferred by subtracting the absorption patterns in the spectrum of **10** from the absorption patterns in the corresponding spectra of the mixture of **10** and **11**, given above. However, separation of **10** and **11** was possible by GC/MS: mass spectrum of **11** (70 eV), m/e (relative intensity), 190.1 (M+2, 4.7), 189.2 (M+1, 5.7), 188.2 (molecular ion, 49.3), 146.1 (22.9), 127.1 (10.8), 115.1 (15.8), 114.1 (100.0), 113.1 (71.4), 106.1 (35.1), 99.1 (54.2), 87.1 (17.8), 85.1 (18.7), 81.1 (25.3), 79.1 (28.7), 77.1 (10.7), 74.1 (13.4), 73.1 (18.3), 71.1 (20.3), 65.1 (11.2), 60.1 (11.0), 59.1 (42.8), 58.1 (19.8), 55.1 (10.2), 53.1 (24.4), 47.1 (22.9), 46.1 (19.9), 45.1 (55.3), 41.1 (68.1).

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Registry No. **2**, 87830-51-1; **5a**, 100296-39-7; **5b**, 100206-70-0; **6a**, 100206-72-2; **6b**, 100296-02-4; **7**, 100206-74-4; **8**, 100206-73-3; **9** (isomer 1), 100206-76-6; **9** (isomer 2), 100296-04-6; **10**, 100206-77-7; **11**, 100206-78-8; 5-hexen-2-one, 109-49-9; 1,3-propanedithiol, 109-80-8; boron trifluoride etherate, 109-63-7; methanethiol, 74-93-1.

Supplementary Material Available: A list of atomic positional parameters, thermal parameters, and hydrogen atomic parameters for **9a** (3 pages). Ordering information is given on any current masthead page.

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Reactions of *o*-Quinone Monoimides with Sulfoxides, Diazoalkanes, and Triphenylphosphine

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o-Quinone monoimides react with dialkyl sulfoxides to produce *N*-(2-(aroyloxy)phenyl)-*S*,*S*-dialkylsulfoximines. Analogously, *o*-quinone diimides and dialkyl sulfoxides combine to form *N*-(2-(dibenzoylamino)phenyl)-*S*,*S*-dialkylsulfoximines. *o*-Quinone monoimides when admixed with phenyldiazomethane and diphenyldiazomethane afford 2-(aroyloxy)-*N*-(phenylmethylene)- and 2-(aroyloxy)-*N*-(diphenylmethylene)benzenamines. Similarly, *o*-quinone monoimides treated with ethyl diazoacetate form 2-(aroyloxy)-*N*-(carbethoxymethylene)benzenamines. *o*-Quinone monoimides are converted by triphenylphosphine into benzoxazoles.

Until recently only two publications on the reactions of *o*-quinone monoimides had appeared. Adams and Stewart[1] reported that hydrogen chloride added 1,4 across the enimide system of **1** to produce **2** (Scheme I). Mustafa and Kamel[2] described the twofold addition of arylmagnesium bromides to the carbonyl and imido moieties of **3** which gave rise to **4**. In 1984[3] we demonstrated that **5** underwent Diels–Alder reactions across the heterodiene system with

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