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Facile Syntheses of Allylic Allenethiosulfinates and -sulfonates, and of β-Iodo α,β-Unsaturated γ-Sultines

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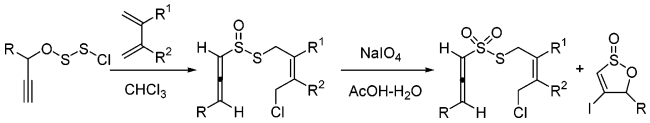
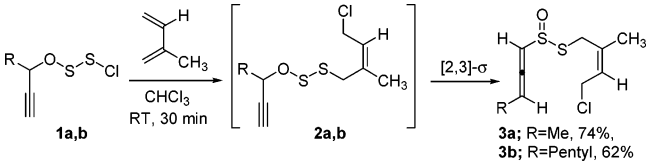


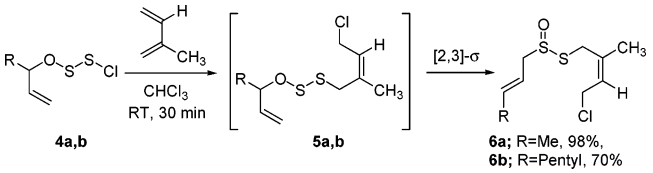
The regiospecificity of the 1,4-addition of the recently reported novel alkoxy chlorodisulfides to 2-methyl-1,3-butadiene has been established. Allyl allenethiosulfinates formed by spontaneous [2,3]-sigmatropic rearrangement of the addition products were oxidized at 4 °C to the corresponding thiosulfonates. Periodate oxidation at room temperature, preferably in the presence of I_2, resulted in oxidative cleavage and cyclization to β-iodo α,β-unsaturated γ-sultines. Such sultines, with varying degrees of γ-alkyl substitution, were also conveniently prepared by reaction of iodine with alkyl allenesulfinates.

Within the framework of our ongoing studies of the chemistry of novel organosulfur compounds,[1] we recently reported the first successful synthesis and characterization of propargyloxy and allyloxy chlorodisulfides (ROSSCl).[2] While these compounds were found to be reasonably stable in chloroform solution at −18 °C, they decomposed rapidly when isolated at room temperature. However, the synthetic potential of α-alkyl-substituted representatives of these structures was demonstrated by their 1,4-addition to the nucleophilic diene 2,3-dimethyl-1,3-butadiene and subsequent spontaneous [2,3]-sigmatropic rearrangement to substituted allyl allenethiosulfinates and substituted allyl 2-propene-1-thiosulfinates, respectively.[2] Such compounds are derivatives of allicin (allyl 2-propene-1-thiosulfinate), which has been isolated from common garlic, *Allium sativum*, and has been found to have remarkable medicinal properties.[3] The compound shows antibacterial and antiviral activity, as well as tumor-inhibiting and fungicidal properties. The relatively facile synthesis of large numbers of related compounds and the screening of their biological activities are therefore of obvious importance, and our reported findings facilitated such work. Herein, we report on extensions of our investigation.

SCHEME 1



SCHEME 2



To examine the regioselectivity of the addition of alkoxy chlorodisulfides to *unsymmetrical* 1,3-dienes, we reacted α-methylpropargyloxy chlorodisulfide, **1a**, with isoprene at room temperature in the manner described for the reaction with 2,3-dimethyl-1,3-butadiene (see Scheme 1).[2] As in the latter case, the product isolated was an *S*-allyl allenethiosulfinate ester, specifically **3a** (74% yield), which was formed by 1,4-addition of **1a** to the diene, followed by a [2,3]-sigmatropic rearrangement of the thiosulfoxylate **2a**. The thiosulfinate **3a** incorporates two chiral elements, the thiosulfinate and the allene functions, and was in fact obtained as a mixture of two diastereoisomers in the ratio of 1.4:1. Likewise, the reaction of α-pentylpropargyloxy chlorodisulfide **1b** with isoprene led, presumably via **2b**, to a mixture of two diastereoisomers of the thiosulfinate **3b** (isolated in 62% yield in the ratio of 1.1:1).

In an analogous manner, the in situ reaction of α-methylallyloxy and α-pentylallyloxy chlorodisulfide (**4a**, **4b**, respectively) with isoprene led via 1,4-addition (**5a**, **5b**) and [2,3]-sigmatropic rearrangement, to the *S*-allyl allylthiosulfinate esters **6a** (98% yield) and **6b** (70% yield), respectively (Scheme 2).

The structures of the obtained thiosulfinates (**3a**, **3b**, **6a**, **6b**) led to the conclusion that in all four cases the 1,4-addition of the alkoxy chlorodisulfide to 2-methyl-1,3-diene (isoprene) proceeds in a regiospecific manner to yield the isomer in which the sulfur function is bonded to C-1 of the 2-methyl-2-butenyl moiety and the chlorine atom to C-4. These observations for chlorodisulfides are consistent with those reported for the reactions of sulfenyl chlorides with 1,3-dienes.[4] In those cases, the kinetically controlled product at low temperatures is a 1,2-adduct produced via a thiiranium chloride ion pair intermediate (presumably the result of π-electron nucleophilic displacement of chlorine from the sulfur). The 1,2-adduct is in equilibrium with the thiiranium chloride which, at room temperature, converts to the thermodynamically preferred 1,4-adduct. The formation of the thiiranium intermediate and its conversion to the 1,4-adduct involves partial positive charge on C-2 and favors the product in which, in the case of isoprene, the methyl-bearing

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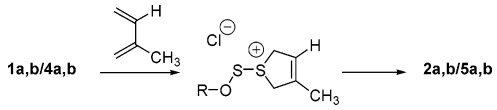
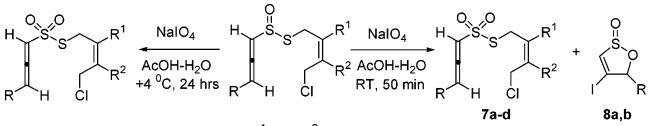
SCHEME 3



SCHEME 4



7a; 94%, **7b;** 87%,[b] **7c;** 87%, **7d;** 76%

3a; R=R[1]=Me, R[2]=H, **3b;** R=Pentyl, R[1]=Me, R[2]=H, **3c;** R=R[1]=R[2]=Me, **3d;** R=Pentyl, R[1]=R[2]=Me

7a (48%):**8a** (25%) = 1.96:1, **7b** (31%):**8b** (19%) = 1.66:1,[a] **7c** (38%):**8a** (20%) = 1.93:1, **7d** (26%):**8b** (32%) = 1:1.24

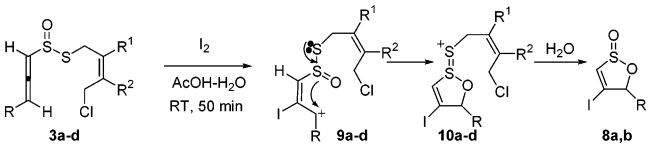
[a] Reaction time is 20 h due to the low solubility of the thiosulfinate **3b**. [b]Reaction time is 5 days due to the low solubility of the thiosulfinate **3b**.

carbon is vicinal to the sulfur-bearing one. In the absence of contradictory evidence, we assume that the mechanism of alkoxy chlorodisulfide addition to 1,3-dienes proceeds by a similar mechanism. As we worked at room temperature, the isolation of the 1,4-adduct is not surprising. However, whereas 1,4-adducts from the addition of sulfenyl chlorides to 1,3-dienes were generally found to be the more stable *E*-olefins,[4] especially in nonpolar medium,[4a−c] we found the products **3a**, **3b**, **6a**, and **6b** to have the *Z* configuration. Should this not be the more stable configuration of these products (i.e., the methyl substituent does not reverse the relative stability), then it is conceivable that the stereochemistry of our products is the result of their formation via a five-membered ring sulfonium intermediate, as shown in Scheme 3. The formation of such an intermediate in the case of alkoxy chlorodisulfide addition to 1,3-dienes, while an analogous intermediate does not appear to be usually formed in the case of sulfenyl chloride additon,[4] may be rationalized as the result of the greater nucleophilicity of the distal sulfur atom in the former case ("α effect") than the sulfur atom in the latter. Subsequent preferred nucleophilic attack of the chloride ion on the less hindered of the CH_2 groupings of the five membered ring is to be expected. The previously reported 1,4-addition of propargyloxy and allyloxy chlorodisulfides to 2,3-dimethyl-1,3-butadiene, which also yielded products of *Z* configuration, may be rationalized in a similar manner.[2]

The above-mentioned four thiosulfinates derived from isoprene were found to be much more stable at room temperature than the analogous ones (**3c**,**d**, Scheme 4), derived from 2,3-dimethyl-1,3-butadiene.[2] This is of significance in view of the known low stability of allicin derivatives in general, on one hand, and their potential medicinal value on the other.

As the next step in our quest for more stable derivatives of potential medicinal interest, we decided to oxidize some of the *S*-allyl allenethiosulfinates at hand, namely **3a**−**d**, to the corresponding thiosulfonates. Oae and co-workers[5,6] have studied the oxidation of thiosulfinic *S*-esters with various oxidants. They reported that these fall into two categories.[5c] To the first belong oxidants such as peracids and N_2O_4 which oxidize the sulfenyl sulfur and whose action leads to cleavage

SCHEME 5



of the S−S bond and further oxidation of both moieties. These were labeled "electrophilic" oxidants, and their mode of action was described as being initiated by the nucleophilic attack of the divalent sulfur on the peroxy oxygen of the peracid (for example). Sodium metaperiodate (in aqueous organic solvents in the presence of acid catalysis) was presented as the outstanding example of the second category, though sodium iodate, selenium dioxide, sodium chlorate, and potassium permanganate were also listed.[5c] These oxidants were reported to selectively oxidize thiosulfinates at the sulfinyl sulfur to the coresponding thiosulfonates and not to cause cleavage of the S−S bond. The mechanism of action of the second category, classified as "nucleophilic" oxidants, was postulated to proceed by nucleophilic attack of, for example, a periodate oxygen on the sulfinyl electrophilic center. However, it appears to us that some of the reported findings relating to this selective oxidation of thiosulfinates to thiosulfonates are not easily rationalized within the framework of the proposed "nucleophilic" oxidation mechanism. Rather, we suggest that the reported specificity of periodate and others of its kind is best explained by a mechanism of electron transfer from the S−S−O triad. In such an electron-depleted triad the electrophilic center subject to water addition would of course be the sulfinyl sulfur.

In the event, when periodate oxidation of **3a**−**d** was carried out at 4 °C the corresponding thiosulfonate esters **7a**−**d** were obtained in good yield (76−94%). On the other hand, when Oae's conditions[5b] were used, only limited yields of **7a**−**d** were isolated, and these were accompanied in each case by a considerable amount of another product from which they were separated by chromatography. The additional products were identified by full spectral analysis as the *β*-iodo α,*β*-unsaturated *γ*-sultine **8a**, derived from **3a** as well as from **3c**, and as **8b**, derived from **3b** and from **3d** (Scheme 4). Compounds **8a** and **8b** were obtained as a mixture of two diastereoisomers in the ratio of 1:1 as a consequence of the chirality of the sulfur and of C-5. (Attempted oxidation of **3** with $KMnO_4$ led to extensive decomposition due to the poor stability of compounds **3**.)

In the past, we have studied the mechanism and stereochemistry of the formation of *β*-bromo-α,*β*-unsaturated *γ*-sultines by reaction of alkyl allenesulfinates with bromine.[7] The fragmentation−cyclization mechanism suggested in Scheme 5 for the formation of **8a**,**b** is an adaptation of the conclusion from that study.

In his report on the oxidation of thiosulfinates with periodate Oae already noted the appearance of I_2, which obviously results from further reduction of iodate by available organosulfur compound. It is a similar reaction which, in the present study, on one hand produces the necessary iodine (or iodonium species) to yield the sultines in the amounts isolated, and on the other, reduces the total yield by oxidative destruction. Not unexpectedly it was found that when a solution of **3c** was added dropwise

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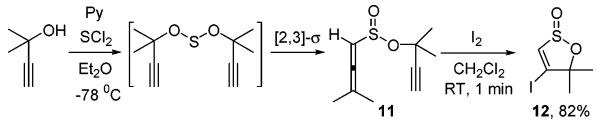
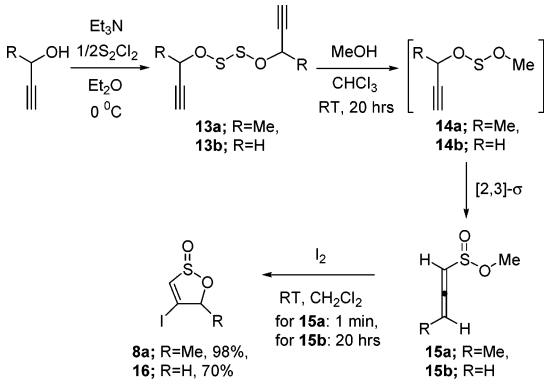
SCHEME 6



SCHEME 7



at room temperature to an aqueous acetic acid solution of two equivalents each of sodium metaperiodate and iodine, only the sultine **8a** was produced.

The present newly encountered β-iodo α,β-unsaturated γ-sultines have the advantage over their previously synthesized β-bromo-α,β-unsaturated γ-sultine analogues in that the iodine is more readily replaced by various substituents and functional groups than bromine. This potential is of importance in preparing candidates for biological testing, keeping in mind the well-known biological activity of γ-butenolides[8]—the carbon analogues of our α,β-unsaturated γ-sultines. Recently the biological activity of γ-sultines has also been reported.[9] Though the reaction of I_2 with normal olefinic bonds is not a generally useful reaction, the above formation of sultines **8a**,**b** suggests that the higher energy allene π-bonds do not suffer such limitation. We were therefore prompted to check if iodo sultines could be synthesized in a more direct fashion from more readily prepared and stable starting materials, in the same way that we prepared the β-bromo α,β-unsaturated γ-sultines in the past, namely by direct reaction of I_2 with allenesulfinate esters.

In fact, we found this general route to be surprisingly easy and effective. To obtain a γ,γ-dialkylsultine such as β-iodo α,β-unsaturated γ,γ-dimethyl-γ-sultine **12** in quantitative yield it was most convenient to react the readily available 2-methylbut-3-yn-2-yl 3-methylbuta-1,2-diene 1-sulfinate **11**[10] with I_2 in CH_2Cl_2 solution for 1 min at room temperature (Scheme 6). To obtain the γ-monoalkyl or the γ-unsubstituted sultines, it was found advantageous to react the iodine with the appropriate methyl allenesulfinate **15**, prepared[11] as shown in Scheme 7. The terminally unsubstituted, and therefore less nucleophilic, β,γ-double bond of the allene **15b** required a much longer reaction time (20 h compared to only 1 min for **15a**).

Experimental Section

***S*-[(2*Z*)-4-Chloro-2-methylbut-2-enyl]buta-1,2-diene-1-sulfinothioate (3a):** mixture of two diastereoisomers in the ratio of 1.4:1 (yield 74%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.22 (dq, J = 6.0, 3.0 Hz, 1H for both isomers), 5.90 (qd, J = 7.5, 6.0 Hz, 1H for both isomers), 5.68 (triplet of multiplet, J = 8.0 Hz, 1H for both isomers), AB system: 4.19 and 4.13 (dd, J = 11.0, 8.0 Hz, 1H each for both isomers), ABq: 3.92 and 3.69 (d, J = 13.0 Hz, 1H each, for one isomer), ABq: 3.92 and 3.68 (d, J = 13.0 Hz, 1H each, for the other isomer), 1.92 (br s, 3H for both isomers), 1.87 and 1.84 (dd, J = 7.5, 3.0 Hz, 3H each); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.12 and 203.05 (=*C*= each), 136.41 and 136.38 (=*C*− each), 125.87 (=*C*H− for both isomers), 100.95 and 100.85 (*C*H= each), 97.48 and 97.37 (*C*H= each), 39.94 (−*C*H$_2$− for both isomers), 33.11 and 33.06 (−*C*H$_2$− each), 22.73 (*C*H$_3$− for both isomers), 13.90 and 13.76 (*C*H$_3$− each); IR (neat) 1080, 1446, 1691, 1943, 2975 cm^{-1}; MS (CI/CH_4) m/z 239 (MH$^+$ ($C_9H_{14}OS_2{}^{37}Cl$), 2), 237 (MH$^+$ ($C_9H_{14}OS_2{}^{35}Cl$), 8), 135 ($ClCH_2$-CH=C(CH_3)-CH=SH$^+$, 27), 99 (100); HRMS (elemental composition) calcd ($C_9H_{14}OS_2{}^{35}Cl$) 237.0175, found 237.0174, calcd ($C_9H_{14}OS_2{}^{37}Cl$) 239.0145, found 239.0154.

***S*-[(2*Z*)-4-Chloro-2-methylbut-2-enyl]octa-1,2-diene-1-sulfinothioate (3b):** mixture of two diastereoisomers in the ratio of 1.1:1 (yield 62%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.254 and 6.250 (dt, J = 6.0, 3.0 Hz, 1H each), 5.93 and 5.91 (q, J = 6.0 Hz, 1H each), 5.67 (triplet of multiplet, J = 8.0 Hz, 1H for both isomers), AB system: 4.19 and 4.13 (dd, J = 11.0, 0.8 Hz, 1H each, for both isomers), AB system for one isomer: 3.920 (dd, J = 13.0, 0.8 Hz, 1H) and 3.678 (d, J = 13.0 Hz, 1H), AB system for the other isomer: 3.918 (dd, J = 13.0, 0.8 Hz, 1H) and 3.678 (d, J = 13.0 Hz, 1H), 2.23−2.12 (m, 2H for both isomers), 1.92 (br s, 3H for both isomers), 1.52−1.43 (m, 2H for both isomers), 1.36−1.28 (m, 4H for both isomers), 0.92−0.87 (m, 3H for both isomers); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.31 and 202.26 (=*C*= each), 136.47 and 136.44 (=*C*− each), 125.86 (=*C*H− for both isomers), 102.62 (*C*H= for both isomers), 101.49 and 101.38 (*C*H= each), 39.97 (−*C*H$_2$− for both isomers), 33.17 (−*C*H$_2$− for both isomers), 31.26 and 31.23 (−*C*H$_2$− each), 28.41 and 28.33 (−*C*H$_2$− each), 28.24 (−*C*H$_2$− for both isomers), 22.74 (*C*H$_3$− for both isomers), 22.47 (−*C*H$_2$− for both isomers), 14.11 (*C*H$_3$− for both isomers); IR (neat): 1080, 1094, 1455, 1693, 1947, 2928 cm^{-1}; MS (CI/CH_4) m/z 292 (M$^+$, 4), 249 (M$^+$ − C_3H_7, 32), 135 ($ClCH_2$-CH=C(CH_3)-CH=SH$^+$, 46), 99 (94.76); HRMS (elemental composition) calcd ($C_{13}H_{21}OS_2{}^{35}Cl$) 292.0722, found 292.0716.

***S*-[(2*Z*)-4-Chloro-2-methylbut-2-enyl] (2*E*)-but-2-ene-1-sulfinothioate (6a):** yield 98%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (dqt, J = 15.3, 6.5, 1.0 Hz, 1H), 5.65 (triplet of multiplet, J = 8.0 Hz, 1H), 5.58 (dtq, J = 15.3, 7.5, 1.8 Hz, 1H), AB system: 4.18 and 4.12 (ddq, J = 12.0, 8.0, 1.0 Hz, 1H each), AB system: 3.90 (dd, J = 13.0, 0.8 Hz, 1H each), and 3.68 (d, J = 13.0 Hz, 1H each), AB system: 3.80 and 3.73 (ddquint, J = 13.0, 7.5, 1.0 Hz, 1H each), 1.91 (dt, J = 1.5, 0.8 Hz, 3H), 1.79 (ddt, J = 6.5, 1.8, 0.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.55 (=*C*−), 136.12 (=*C*H−), 125.67 (=*C*H−), 118.36 (=*C*H−), 59.34 (−*C*H$_2$−), 39.90 (−*C*H$_2$−), 32.58 (−*C*H$_2$−), 22.57 (*C*H$_3$−), 18.31 (*C*H$_3$−); IR (neat) 1075, 1092, 1446, 1664, 2970 cm^{-1}; MS (CI/CH_4) m/z 241 (MH$^+$ ($C_9H_{16}OS_2{}^{37}Cl$), 0.4), 239 (MH$^+$ ($C_9H_{16}OS_2{}^{35}Cl$), 2), 203 ((M − Cl)$^+$, 0.7), 135 ($ClCH_2$-CH=C(CH_3)-CH=SH$^+$, 42), 103 (CH_3CH=$CHCH_2$S=O$^+$, 79), 99 (100); HRMS (elemental composition) calcd ($C_9H_{16}OS_2{}^{37}Cl$) 241.0302, found 241.0303, calcd ($C_9H_{16}OS_2{}^{35}Cl$) 239.0331, found 239.0334.

***S*-[(2*Z*)-4-Chloro-2-methylbut-2-enyl] (2*E*)-oct-2-ene-1-sulfinothioate (6b):** yield 70%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86 (dtt, J = 15.3, 6.5, 1.0 Hz, 1H), 5.65 (triplet of multiplet, J = 8.0 Hz, 1H), 5.54 (dtt, J = 15.3, 7.5, 1.8 Hz, 1H), AB system: 4.18 and 4.12 (ddq, J = 12.0, 8.0, 1.0 Hz, 1H each), AB system: 3.90 and 3.68 (dd, J = 13.0, 0.8 Hz, 1H each), AB system: 3.82 and 3.74 (ddq, J = 13.0, 7.5, 1.0 Hz, 1H each), 2.11 (br q, J = 7.5, Hz, 2H), 1.90 (dt, J = 1.5, 0.8 Hz, 3H), 1.45−1.36 (m, 2H), 1.32−1.27 (m, 4H), 0.91−0.86 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.54 (=*C*H−), 136.57 (=*C*−), 125.67 (=*C*H−), 116.98

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(=*C*H−), 59.45 (−*C*H_2−), 39.90 (−*C*H_2−), 32.68 (−*C*H_2−), 32.55 (−*C*H_2−), 31.33 (−*C*H_2−), 28.56 (−*C*H_2−), 22.57 (*C*H_3−), 22.50 (−*C*H_2−), 14.09 (*C*H_3−); IR (neat) 1083, 1455, 1660, 2927 cm^{-1}; MS (CI/CH_4) *m*/*z* 297 (MH^+ ($C_{13}H_{24}OS_2{}^{37}Cl$), 3), 295 ($MH^+$ ($C_{13}H_{24}OS_2{}^{35}Cl$), 5), 159 ($CH_3(CH_2)_4CH{=}CHCH_2S{=}O^+$, 68), 135 ($ClCH_2$-CH=C($CH_3$)-CH=$SH^+$, 12), 111 ($CH_3(CH_2)_4CH{=}CHCH_2^+$, 46), 99 (38); HRMS (elemental composition) calcd ($C_{13}H_{24}OS_2{}^{37}Cl$) 297.0928, found 297.0935, calcd ($C_{13}H_{24}OS_2{}^{35}Cl$) 295.0957, found 295.0957.

***S*-[(2*Z*)-4-Chloro-2-methylbut-2-enyl] buta-1,2-diene-1-sulfonothioate (7a):** see Scheme 4; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.34 (dq, J = 6.0, 3.0 Hz, 1H), 6.00 (qd, J = 7.5, 6.0 Hz, 1H), 5.68 (triplet of multiplet, J = 8.0 Hz, 1H), 4.13 (dq, J = 8.0, 0.8 Hz, 2H), AB system: 3.86 and 3.81 (dd, J = 13.0, 0.8 Hz, 1H each), 1.907 (dt, J = 1.5, 0.8 Hz, 3H), 1.906 (dd, J = 7.5, 3.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.45 (=*C*=), 134.51 (=*C*−), 126.63 (=*C*H−), 104.29 (*C*H=), 97.88 (*C*H=), 39.50 (−*C*H_2−), 37.05 (−*C*H_2−), 22.54 (*C*H_3−), 13.63 (*C*H_3−); IR (neat) 1126, 1326, 1952, 2928 cm^{-1}; MS (CI/CH_4) *m*/*z* 253 (MH^+, 2), 217 ($(M - Cl)^+$, 24), 135 ($ClCH_2$-CH=C(CH_3)-CH=SH^+, 48), 99 (100); HRMS (elemental composition) calcd ($C_9H_{14}O_2S_2{}^{35}Cl$) 253.0124, found 253.0125.

***S*-[(2*Z*)-4-Chloro-2-methylbut-2-enyl] octa-1,2-diene-1-sulfonothioate (7b):** see Scheme 4; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.36 (dt, J = 6.0, 3.0 Hz, 1H), 6.03 (td, J = 7.5, 6.0 Hz, 1H), 5.69 (triplet of multiplet, J = 8.0 Hz, 1H), 4.13 (d, J = 8.0 Hz, 2H), ABq: 3.86 and 3.80 (d, J = 13.0 Hz, 1H each), 2.23 (qd, J = 7.5, 3.0 Hz, 2H), 1.91 (dt, J = 1.5, 0.8 Hz, 3H), 1.54−1.45 (m, 2H), 1.37−1.32 (m, 4H), 0.92−0.88 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.88 (=**C**=), 134.63 (=**C**-), 126.65 (=*C*H-), 104.91 (*C*H=), 103.12 (*C*H=), 39.55 (−*C*H_2−), 37.05 (−*C*H_2−), 31.13 (−*C*H_2−), 28.24 (−*C*H_2−), 28.13 (−*C*H_2−), 22.58 (*C*H_3−), 22.34 (−*C*H_2−), 13.98 (*C*H_3−); IR (neat) 1127, 1330, 1455, 1952, 2927 cm^{-1}; MS (CI/CH_4) *m*/*z* 309 (MH^+, 2), 307 ($(M - H)^+$, 2), 273 ($(M - Cl)^+$, 7), 135 ($ClCH_2$-CH=C(CH_3)-CH=SH^+, 36), 99 (83.64); HRMS (elemental composition) calcd ($C_{13}H_{22}O_2S_2{}^{35}Cl$) 309.0750, found 309.0751.

***S*-[(2*Z*)-4-Chloro-2,3-dimethylbut-2-enyl] buta-1,2-diene-1-sulfonothioate (7c):** see Scheme 4; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.33 (dq, J = 6.0, 3.0 Hz, 1H), 6.00 (qd, J = 7.5, 6.0 Hz, 1H), 4.11 (br s, 2H), 3.88−3.87 (br m, 2H), 1.91 (dd, J = 7.5, 3.0 Hz, 3H), 1.84 (br s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.61 (=*C*=), 132.55 (=*C*−), 127.77 (=*C*−), 104.00 (=*C*H−), 97.73 (=*C*H−), 45.30 (−*C*H_2−), 39.64 (−*C*H_2−), 18.61 (*C*H_3−), 17.84 (*C*H_3−), 13.73 (*C*H_3−); IR (neat) 1127, 1327, 1952, 2926 cm^{-1}; MS (CI/CH_4) *m*/*z* 267 (MH^+, 1), 231 ($(M - Cl)^+$, 24), 149 (C_6H_{10}-SCl, 43), 113 (100); HRMS (elemental composition) calcd ($C_{10}H_{16}O_2$-$S_2{}^{35}Cl$) 267.0280, found 267.0283.

***S*-[(2*Z*)-4-Chloro-2,3-dimethylbut-2-enyl] octa-1,2-diene-1-sulfonothioate (7d):** see Scheme 4; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.35 (dt, J = 6.0, 3.0 Hz, 1H), 6.02 (td, J = 7.5, 6.0 Hz, 1H), 4.11 (br s, 2H), 3.88−3.87 (br m, 2H), 2.23 (qd, J = 7.5, 3.0 Hz, 2H), 1.84 (s, 6H), 1.34−1.32 (m, 6H), 0.92−0.88 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.00 (=*C*=), 132.55 (=*C*−), 127.83 (=*C*−), 104.60 (=*C*H−), 102.96 (=*C*H−), 45.33 (−*C*H_2−), 39.62 (−*C*H_2−), 31.13 (−*C*H_2−), 28.31 (−*C*H_2−), 28.14 (−*C*H_2−), 22.34 (−*C*H_2−), 18.62 (*C*H_3−), 17.86 (*C*H_3−), 13.98 (*C*H_3−); IR (neat) 1128, 1328, 1952, 2930 cm^{-1}; MS (CI/CH_4) *m*/*z* 323 (MH^+, 2), 321 ($(M - H)^+$, 7), 287 ($(M - Cl)^+$, 26), 149 ($C_6H_{10}SCl$, 70), 113 (100); HRMS (elemental composition): calcd ($C_{14}H_{24}O_2S_2{}^{35}Cl$) 321.0750, found 321.0752.

4-Iodo-5-pentyl-5*H*-1,2-oxathiole 2-Oxide (8b). Obtained as a mixture of two diastereoisomers in a ratio of 1:1 and separated by column chromatography; see Scheme 4. For one isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (d, J = 2.0 Hz, 1H), 5.18 (ddd, J = 8.0, 3.1, 2.0 Hz, 1H), 2.16−2.06 (m, 1H), 1.86 (br quint, J = 7.5 Hz, 1H), 1.56−1.46 (m, 2H), 1.37−1.26 (m, 4H), 0.93−0.86 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.46 (=**C**H−), 107.89 (=**C**-), 99.59 (−**C**H−), 34.43 (−**C**H_2−), 31.24 (−**C**H_2−), 24.25 (−**C**H_2−), 22.34 (−**C**H_2−), 13.98 (−**C**H_3). For the other isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96 (d, J = 2.0 Hz, 1H), 5.57 (ddd, J = 7.2, 3.0, 2.0 Hz, 1H), 2.12−2.03 (m, 1H), 1.72−1.65 (m, 1H), 1.33−1.31 (m, 6H), 0.91−0.87 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.23 (=*C*H−), 109.02 (=*C*−), 96.74 (−*C*H−), 32.70 (−*C*H_2−), 31.23 (−*C*H_2−), 23.21 (−*C*H_2−), 22.40 (−*C*H_2−), 13.95 (−*C*H_3). For both isomers: IR (neat) 1128, 1579, 2930 cm^{-1}; MS (CI/CH_4) *m*/*z* 301 (MH^+, 23), 252 ($(M - SO)^+$, 32), 173 ($(M - I)^+$, 9), 127 (I^+, 9); HRMS (elemental composition) calcd ($C_4H_6O_2SI$) 244.9133, found 244.9129, calcd ($C_8H_{14}O_2SI$) 300.9759, found 300.9764.

Methyl Buta-1,2-diene-1-sulfinate (15a). A mixture of two diastereoisomers in the ratio of 1:1 (yield 51% for two steps starting from the corresponding alcohol): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.931 and 5.929 (dq, J = 6.0, 3.0 Hz, 1H each), 5.79 and 5.77 (qd, J = 7.5, 6.0 Hz, 1H each), 3.71 (s, 3H for both isomers), 1.85 and 1.82 (dd, J = 7.5, 3.0 Hz, 3H each); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.39 and 205.23 (=*C*= each), 101.57 and 101.54 (=*C*H− each), 95.04 and 94.96 (=*C*H− each), 50.43 and 50.34 (*C*H_3− each), 13.47 and 13.42 (*C*H_3− each); IR (neat) 1127, 1450, 1950, 2941 cm^{-1}; MS (CI/CH_4) *m*/*z* 133 (MH^+, 22), 117 ($(M - CH_3)^+$, 20), 101 ($(MH - CH_3OH)^+$, 8); HRMS (elemental composition) calcd ($C_5H_9O_2S$) 133.0323, found 133.0320.

4-Iodo-5,5-dimethyl-5*H*-1,2-oxathiole 2-oxide (12): yield 82%; reaction time 1 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.85 (s, 1H), 1.74 (s, 3H), 1.57 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.41 (=**C**H−), 115.44 (=*C*−), 102.24 (−*C*−), 28.96 (−*C*H_3), 27.33 (−*C*H_3); IR (neat) 1112, 1578, 2989 cm^{-1}; MS (CI/CH_4) *m*/*z* 259 (MH^+, 11), 258 (M^+, 10), 210 ($(M - SO)^+$, 30), 131 ($(M - I)^+$, 38), 86 (73), 84 (100); HRMS (elemental composition) calcd ($C_5H_7O_2SI$) 257.9212, found 257.9212.

4-Iodo-5-methyl-5*H*-1,2-oxathiole 2-Oxide (8a). Obtained as a mixture of two diastereoisomers in a ratio of 1:1 (yield 98%). The reaction time is 1 min. Also see Scheme 4. For one isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.963 (d, J = 2.0 Hz, 1H), 5.25 (qd, J = 7.0, 2.0 Hz, 1H), 1.75 (d, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.61 (=*C*H−), 108.82 (=*C*−), 96.20 (−*C*H-), 22.43 (−*C*H_3). For the other isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.957 (d, J = 2.0 Hz, 1H), 5.64 (qd, J = 7.0, 2.0 Hz, 1H), 1.59 (d, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.06 (=*C*H−), 109.89 (=*C*−), 93.53 (−*C*H−), 19.93 (−*C*H_3). For both isomers: IR (neat) 1123, 1578, 2980 cm^{-1}; MS (CI/CH_4) *m*/*z* 245 (MH^+, 100), 244 (M^+, 32), 196 ($(M - SO)^+$, 88), 127 (I^+, 14), 117 ($(M - I)^+$, 93); HRMS (elemental composition) calcd ($C_4H_5O_2$-SI) 243.9055, found 243.9045.

4-Iodo-5*H*-1,2-oxathiole 2-oxide (16): yield 70%; the reaction time is 20 h; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 (t, J = 2.1 Hz, 1H), AB system: 5.39 and 5.02 (dd, J = 15.0, 2.1 Hz, 1H each); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.37 (=*C*H−), 101.92 (=*C*−), 87.46 (−*C*H_2−); IR (neat) 1122, 1582, 3085 cm^{-1}; MS (CI/CH_4) *m*/*z* 231 (MH^+, 24), 230 (M^+, 63), 182 ($(M - SO)^+$, 100), 127 (I^+, 27), 103 ($(M - I)^+$, 60); HRMS (elemental composition) calcd ($C_3H_3O_2SI$) 229.8899, found 229.8904.

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Supporting Information Available: Experimental Procedures, ^{1}H NMR, and ^{13}C NMR spectra for all new compounds (**3a**,**b**, **6a**,**b**, **7a**−**d**, **8a**,**b**, **12**, **15a**, and **16**). This material is available free of charge via the Internet at http://pubs.acs.org.

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