

Synthesis and Properties of Monocyclic 5*H*-1,2-Oxathioles (Cyclic α,β-Unsaturated Sulfenic Acid Esters)

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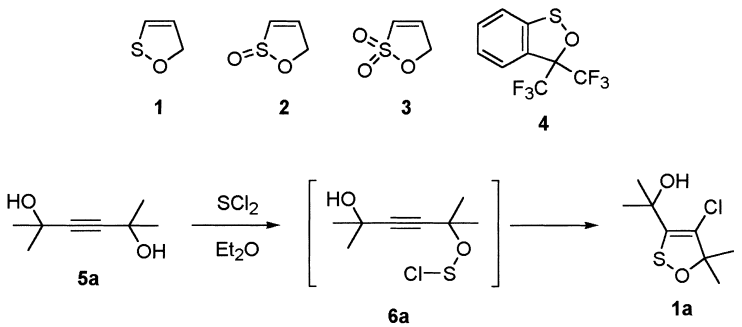
2,5,5-Trimethyl-3-hexyn-2-ol was successively treated with NaH and SCl_2 in Et_2O to provide 3-*t*-butyl-4-chloro-5,5-dimethyl-5*H*-1,2-oxathiole (**1b**), a class of α,β-unsaturated sulfenic acid ester, in 74% yield. Several S-unoxidized 5*H*-1,2-oxathioles were synthesized in similar ways. Analysis by cyclic voltammetry uncovered that the oxidation potentials of **1b**, 3-(1-adamantyl)-4-chloro-5,5-dimethyl-5*H*-1,2-oxathiole (**1c**), and 4-chloro-5,5-dimethyl-3-phenyl-5*H*-1,2-oxathiole (**1d**) are +0.69, +0.68, and +0.78 V, respectively, and are lower than those of sulfides (thioanisole, +0.97 and dimethyl sulfide, +1.09 V), and also lower than that of an acyclic sulfenate ester (ethyl benzenesulfenate, +0.90 V). Thermolysis of **1c** in boiling toluene furnished 2-(1-adamantyl)-3-chloro-4-methylthiophene in 81% yield.

We report here the first synthesis and some properties of monocyclic 5*H*-1,2-oxathioles. To our knowledge, successful synthesis of monocyclic 5*H*-1,2-oxathioles, including the parent compound (**1**), has never been reported.[1] Although a Russian group reported in their deposited document that treatment of 2,5-dimethyl-3-hexyne-2,5-diol (**5a**) with monosulfur dichloride (SCl_2) in Et_2O produced 5*H*-1,2-oxathiole **1a** in 45% yield (Scheme 1), the actual product they obtained is apparently the 2-oxide **2a** (the oxidation product of **1a**) and not **1a**.[2] Thus, the known example of S-unoxidized 5*H*-1,2-oxathioles is limited to a benzo derivative (**4**) reported by J. C. Martin et al.,[3] whereas syntheses of some derivatives of 5*H*-1,2-oxathiole 2-oxide (**2**)[4] and 2,2-dioxide (**3**)[5] were previously reported. 5*H*-1,2-Oxathioles are also of much interest as cyclic esters of α,β-unsaturated sulfenic acids, which are a rare class of compounds.[6] The synthesis of such α,β-unsaturated sulfenate esters, including acyclic ones, has never been reported.[7]

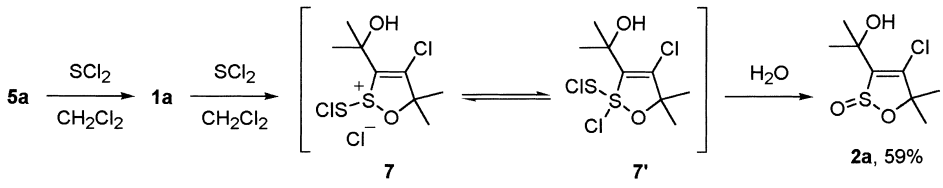
Results and Discussion

We have been investigating the reaction of SCl_2 with acetylenes that carry two bulky alkyl substituents.[8] In this connection, we have re-examined the reaction of **5a** with SCl_2 with the expectation of developing a general synthesis of 5*H*-1,2-oxathioles. The reaction was expected to proceed through the intermediate **6a**, as shown in Scheme 1. Thus, the diol **5a** was treated with 1.5 molar amounts of SCl_2 in CH_2Cl_2 at room temperature without addition of any base. Unexpectedly, however, the reaction gave 5*H*-1,2-oxathiole 2-oxide **2a** in 59% yield and not the expected **1a**, although, as described already, the Russian group claimed that the reaction afforded **1a** in 45% yield.[2] The most probable explanation for the formation of **2a** is the occurrence of a reaction of **1a** with SCl_2 that quickly produces a sulfonium salt intermediate **7** (or an isomeric sulfurane intermediate **7′**), which is finally converted to the 2-oxide **2a** by hydrolysis, probably during work-up procedure (Scheme 2).

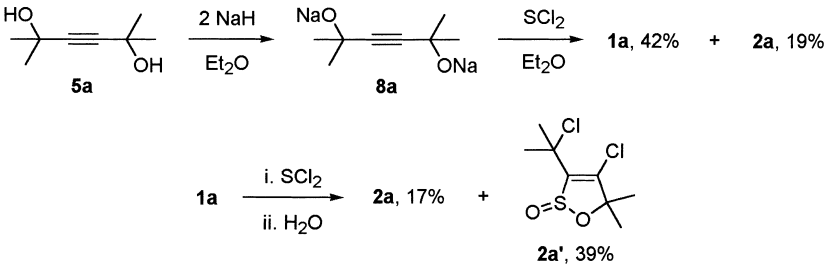
If this is the case, we then could obtain **1a** by enhancing the nucleophilicity of **5a** through conversion to the sodium alcoholate **8a**, thus suppressing the reaction of **1a** with SCl_2. Indeed, when the diol **5a** was treated with SCl_2 in Et_2O, after being converted to **8a** by treatment with NaH in Et_2O, the reaction satisfactorily provided **1a** in 42% yield in addition to **2a** in 19% yield (Scheme 3). Furthermore, in a separate experiment, the reaction of **1a** with 1.5 molar amounts of SCl_2 in CH_2Cl_2 at room temperature, produced 2-oxide **2a** in 17% yield in addi-



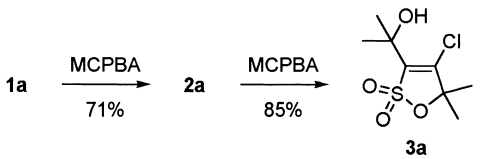
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

tion to 2-oxide **2a′** in 39% yield. The formation of **2a′** is explained as a result of chlorination of the tertiary hydroxy group of **2a** by hydrogen chloride formed mainly by hydrolysis of **7** and excess SCl_2.

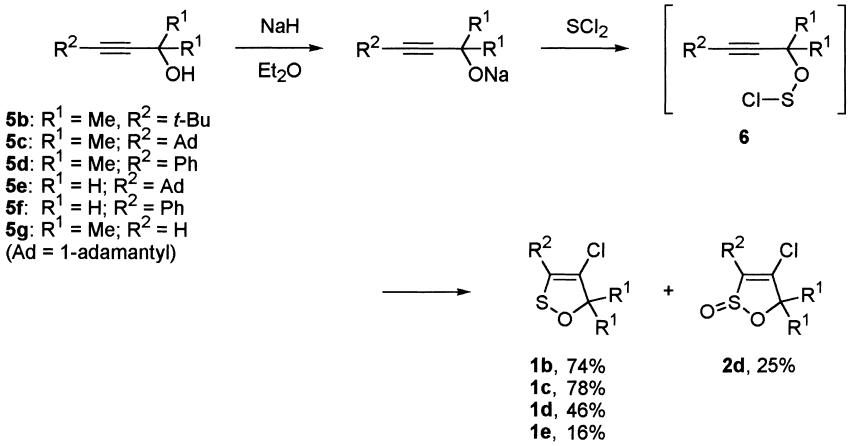
Incidentally, **1a** is oxidized quickly to 2-oxide **2a** in 71% yield by an equimolar amount of *m*-chloroperbenzoic acid (MCPBA), and **2a** is converted to 2,2-dioxide **3a** in 85% yield by further oxidation (Scheme 4).

The presence of two hydroxy groups is unnecessary for the present reaction to take place. Thus, 2,5,5-trimethyl-3-hexyn-2-ol (**5b**) and 4-(1-adamantyl)-2-methyl-3-butyn-2-ol (**5c**) reacted with SCl_2 in Et_2O at room temperature, after treatment with NaH, to give the corresponding 5*H*-1,2-oxathioles **1b** and **1c** in 74 and 78% yields, respectively, while the reaction with 2-methyl-4-phenyl-3-butyn-2-ol (**5d**) with SCl_2 under similar conditions gave **1d** in 46% yield together with 2-oxide **2d** in 25% yield (Scheme 5). The formation of 2-oxide **2d** is explained as the result of the further reaction of **1d** with SCl_2 as discussed above.

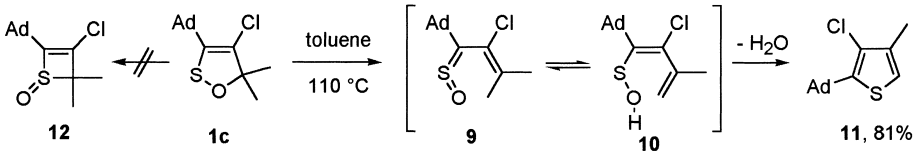
Next, the reaction was applied to less substituted propargyl alcohols. The alcohol **5e** furnished 5*H*-1,2-oxathiole **1e** only in 16% yield, whereas **5f** and **5g** gave complex mixtures from which the expected 5*H*-1,2-oxathioles were not isolated.

Reportedly, the benzo derivative **4** reacts at room temperature within minutes with water or moist air to give sulfinate and other products.[3] In marked contrast, **1a–d** are stable enough to be handled under ordinary experimental conditions; **1a** and **1c** were purified by recrystallization, and **1b** and **1d** by distillation. This would result from kinetic stabilization (steric protection) of the ester part of **1a–d** by a bulky alkyl (or phenyl) substituent at the C-3. Two methyl groups at the C-5 position may partly contribute to the stabilization.

It is documented that, when the S–S bond is placed in a nearly planar ring, the repulsion between unshared electron



Scheme 5.



Scheme 6.

Table 1. The Oxidation Potentials of **1** Obtained by Cyclic Voltammetry[a)]

Compounds	Potentials/V
1b	+0.69
1c	+0.68
1d	+0.78
C_6H_5–S–O–C_2H_5	+0.90
C_6H_5–S–CH_3	+0.97
CH_3–S–CH_3	+1.09

a) Measured in 1.0×10^{-3} M acetonitrile solution containing 0.1 M n-Bu_4NClO_4. Potentials are referred to ferrocene as 0 V. Glassy carbon, Ag/$AgClO_4$, and Pt wire were used for working, reference, and counter electrodes, respectively.

pairs of the sulfur atoms takes place, and lowers the oxidation potential of the compound, thus making it sensitive to oxidation. This would also be true of the S–O bond.[9] Indeed, analysis by cyclic voltammetry revealed that the oxidation of **1b–d** is irreversible, and the oxidation potentials of **1b**, **1c**, and **1d** were +0.69, +0.68, and +0.78 V, respectively, and are lower than those of sulfides (thioanisole, +0.97 and dimethyl sulfide, +1.09 V), and also than that of an acyclic sulfenate ester (ethyl benzenesulfenate, +0.90 V) (Table 1). On the other hand, despite the lower oxidation potentials of **1**, competition experiments showed that oxidation of **1c**, **1d**, and thioanisole by MCPBA to the corresponding S-oxides took place at comparable rates. For example, when equimolar amounts of **1c**, thioanisole, and MCPBA were dissolved in $CDCl_3$, MCPBA was completely consumed within 4 min and gave **3c** and methyl phenyl sulfoxide in the molar ratio 1.2:1.0. The same experiment with **1d** gave **3d** and methyl phenyl sulfoxide in the molar ratio 1.1:1.0. These results demonstrate that steric protection is the major factor of stabilization of **1**.

Some sulfenic acid esters are known to undergo thermal rearrangement to sulfoxides.[10] However, thermolysis of **1c** provided a different result. Thus, heating **1c** in boiling toluene for 24 h gave thiophene **11** in 81% yield (Scheme 6), and rearrangement to sulfoxide **12** did not take place, probably because of increasing ring strains. The mechanism for the formation of **11** would involve the initial cleavage of the C–O bond, and not the S–O bond, to form a thioketone S-oxide intermediate **9**, whose tautomerization to a sulfenic acid **10**, followed by dehydration, would result in the formation of **11**. An analogy to the latter step is found in the formation of a thiophene from an α-oxo-γ,δ-unsaturated thioketone S-oxide.[11,12] Incidentally, 2-oxide **2a** and 2,2-dioxide **3a** are thermally stable and were recovered unchanged when heated under the same conditions.

Experimental

General. Solvents were purified and dried in the usual manner. Silica-gel column chromatography was performed on silica-gel 7734 (Merck, 70–230 mesh). Gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-918 using $CHCl_3$ as the eluent. Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded on a Bruker ARX400 and AM400 spectrometer by using $CDCl_3$ as the solvent with TMS as internal standard. IR spectra were taken on a Perkin-Elmer System 2000 FT-IR spectrometer. Mass spectra were determined on a JEOL JMS-DX303 spectrometer operating at 70 eV in the EI mode. Elemental analyses were performed by the Chemical Analytical Center of Saitama University. Cyclic voltammetry was carried out on an ALS Electrochemical Analyzer Model 660A.

Reaction of 2,5-Dimethyl-3-hexyne-2,5-diol (5a) with SCl_2 without Added Base. Formation of 4-Chloro-α,α,5,5-tetramethyl-5*H*-1,2-oxathiole-3-methanol 2-Oxide (2a). A solution of 155 mg (1.5 mmol) of SCl_2 in CH_2Cl_2 (5 mL) was added to a stirred solution of 143 mg (1.0 mmol) of **5a** in 20 mL of CH_2Cl_2 under argon at room temperature. The reaction was quenched by addition of 10 mL of saturated aqueous $NaHCO_3$ after stirring of 4 h. The organic layer was separated, dried over Na_2SO_4, and evaporated under reduced pressure. The resulting yellow oily residue that contains a small amount of the starting material **5a** was chromatographed on a column of silica-gel with Et_2O as the eluent to give 123 mg (59%) of **2a**: colorless needles (from hexane); mp 95–96 °C; ^{1}H NMR δ 1.54 (3H, s), 1.62 (3H, s), 1.69 (3H, s), 1.72 (3H, s), 3.02 (1H, s); ^{13}C NMR δ 26.67, 28.40, 29.02, 29.58, 71.11, 99.93, 139.96, 148.99; IR (KBr) ν 3350 (O–H), 1095 cm^{-1} (S=O); MS m/z 226, 224 (M^+). Found: C, 42.98; H, 5.79%. Calcd for $C_8H_{13}ClO_3S$: C, 42.76; H, 5.83%.

Reaction of 2,5-Dimethyl-3-hexyne-2,5-diol (5a) with SCl_2 by Using NaH as the Base. Preparation of 4-Chloro-α,α,5,5-tetramethyl-5*H*-1,2-oxathiole-3-methanol (1a). To a stirred suspension of 266 mg (11.1 mmol) of NaH in 95 mL of Et_2O was added 711 mg (5.0 mmol) of **5a** under argon at room temperature. The mixture was stirred for 1 h, and then 518 mg (5.0 mmol) of SCl_2 in 5 mL of Et_2O was added. The reaction was quenched by addition of 100 mL of water after stirring of 5 h. The organic layer and ether extracts (2×40 mL) were combined, washed with water, dried over $MgSO_4$, and evaporated to give the brown oily residue, which was chromatographed on a column of silica-gel. The column was eluted with CH_2Cl_2 and then with CH_2Cl_2/Et_2O (1:1) to give 436 mg (42%) of **1a** and 217 mg (19%) of **2a**. **1a**: Fine colorless needles (from hexane); mp 68 °C; ^{1}H NMR δ 1.45 (6H, s), 1.62 (6H, s), 2.22 (1H, br s); ^{13}C NMR δ 23.82, 27.95, 72.16, 96.56, 107.22, 144.49; IR (KBr) ν 3392 cm^{-1} (O–H); MS m/z 210, 208 (M^+). Found: C, 46.20; H, 6.26%. Calcd for $C_8H_{13}ClO_2S$: C, 46.04; H, 6.28%.

Preparation of 3-*t*-Butyl-4-chloro-5,5-dimethyl-5*H*-1,2-ox-

athiole (1b). To a stirred suspension of 40.0 mg (1.0 mmol) of NaH in 18 mL of Et_2O was added a solution of 141 mg (1.0 mmol) of 2,5,5-trimethyl-3-hexyn-2-ol (**5b**) in Et_2O (2 mL) under argon at room temperature. The stirring was continued for 1 h, and then 104 mg (1.0 mmol) of SCl_2 in 4 mL of Et_2O was added. The reaction was quenched by addition of 20 mL of water after stirring of 1 h. The organic layer and ether extracts (2 × 10 mL) were combined, washed with water, dried over $MgSO_4$, and evaporated. The resulting brown oily residue was chromatographed on a column of silica-gel with pentane as the eluent to give 153 mg (74%) of **1b**: yellow oil; bp 52–55 °C/0.2 mmHg (bulb-to-bulb distillation); ^{1}H NMR δ 1.27 (9H, s), 1.42 (6H, s); ^{13}C NMR δ 23.66, 28.18, 35.59, 95.64, 109.18, 142.86; MS *m/z* 208, 206 (M^+). Found: C, 51.90; H, 7.30%. Calcd for $C_9H_{15}ClOS$: C, 52.29; H, 7.31%.

Preparation of 3-(1-Adamantyl)-4-chloro-5,5-dimethyl-5*H*-1,2-oxathiole (1c). The reaction was carried out using 4-(1-adamantyl)-2-methyl-3-butyn-2-ol (**5c**) as the starting material in a manner similar to that on **1b**. This produced **1c** in 78% yield: pale yellow crystals (from MeCN); mp 72–73 °C; ^{1}H NMR δ 1.41 (6H, s), 1.72 (6H, br s), 2.00 (9H, br s); ^{13}C NMR δ 23.63, 28.35, 36.35, 36.53, 39.49, 95.58, 108.40, 143.06; MS *m/z* 286, 284 (M^+). Found: C, 63.04; H, 7.59%. Calcd for $C_{15}H_{21}ClOS$: C, 63.25; H, 7.43%.

Preparation of 4-Chloro-5,5-dimethyl-3-phenyl-5*H*-1,2-oxathiole (1d) and the 2-Oxide Derivative (2d). The reaction was carried out using 2-methyl-4-phenyl-3-butyn-2-ol (**5d**) as the starting material in an analogous manner to that on **1b**. This produced **1d** and **2d** in 46 and 25% yields, respectively, with 23% recovery of **5d**. **1d**: Pale yellow oil; bp 68–70 °C/0.2 mmHg (bulb-to-bulb distillation); ^{1}H NMR δ 1.56 (6H, s), 7.34–7.42 (3H, m), 7.51 (2H, dd, J = 8.1, 1.6 Hz); ^{13}C NMR δ 23.54, 95.98, 111.85, 128.14, 128.60, 128.75, 129.41, 133.10; MS *m/z* 228, 226 (M^+). Found: C, 58.22; H, 4.82%. Calcd for $C_{11}H_{11}ClOS$: C, 58.27; H, 4.89%. **2d**: colorless oil; bp 95–100 °C/0.5 mmHg (bulb-to-bulb distillation); ^{1}H NMR δ 1.65 (3H, s), 1.84 (3H, s), 7.42–7.49 (3H, m), 7.66–7.69 (2H, m); ^{13}C NMR δ 26.79, 29.04, 99.25, 127.41, 128.48, 128.92, 129.78, 141.09, 141.93; IR (neat) ν 1130 cm^{-1} (S=O). Found: C, 54.28; H, 4.48%. Calcd for $C_{15}H_{21}ClOS$: C, 54.43; H, 4.57%.

Preparation of 3-(1-Adamantyl)-4-chloro-5*H*-1,2-oxathiole (1e). This compound was prepared in 16% yield in a manner similar to that described on **1b** using 3-(1-adamantyl)-2-propyn-1-ol (**5e**) as the starting material: yellow oil; ^{1}H NMR δ 1.72 (6H, br s), 2.01 (9H, br s), 4.85 (2H, s); ^{13}C NMR δ 28.24, 36.35, 36.77, 39.76, 82.97, 99.93, 145.03; MS *m/z* 258, 256 (M^+). HRMS *m/z* 256.0685 (M^+), $C_{13}H_{17}{}^{35}ClOS$ requires 256.0689.

Oxidation of the 5*H*-1,2-Oxathiole 1a. *(a) With SCl_2.* A solution of 30.8 mg (0.3 mmol) of SCl_2 in 0.2 mL of CH_2Cl_2 was added to a solution of 41.7 mg (0.2 mmol) of **1a** in 2 mL of CH_2Cl_2. After stirring for 0.5 h, the reaction was quenched by addition 4 mL of CH_2Cl_2 and 4 mL of aqueous Na_2CO_3. The organic layer and CH_2Cl_2 extracts were combined, washed with water, dried over $MgSO_4$, and evaporated. The yellow oily residue was chromatographed on a column of silica-gel with hexane/CH_2Cl_2 (1:1) as the eluent, and then further purified by GPC and HPLC (CH_2Cl_2) to provide 7.8 mg (17%) of **2a** and 19.0 mg (39%) of **2a′**. **2a′**: Colorless oil, bp 75–76 °C/0.3 mmHg (bulb-to-bulb distillation); ^{1}H NMR δ 1.57 (3H, s), 1.76 (3H, s), 2.02 (3H, s), 2.06 (3H, s); ^{13}C NMR δ 26.70, 29.06, 32.33, 32.83, 64.10, 100.38, 142.73, 146.53; IR (neat) ν 1133 cm^{-1} (S=O); MS *m/z* 246, 244, 242 (M^+). Found: C, 39.58; H, 4.89%. Calcd for $C_8H_{12}Cl_2O_2S$: C, 39.52; H, 4.97%.

(b) With MCPBA. Oxidation of 37.2 mg (0.2 mmol) of **1a** with 44.1 mg (0.2 mmol) of MCPBA in 2 mL of Et_2O at room temperature for 0.5 h produced 28.6 mg (71%) of **2a**.

Oxidation of the 5*H*-1,2-Oxathiole 2-Oxide 2a to the 2,2-Dioxide 3a. 44.9 mg (0.2 mmol) of **2a** was oxidized with 148 mg (0.6 mmol) of MCPBA in 5 mL of Et_2O at room temperature for 22 h. The oxidation furnished 41.0 mg (85%) of **3a**: colorless needles (from hexane); mp 74–75 °C; ^{1}H NMR δ 1.66 (6H, s), 1.69 (6H, s), 2.67 (1H, s); ^{13}C NMR δ 25.55, 28.43, 70.66, 88.44, 138.43, 142.17; IR (KBr) ν 3513 (O–H), 3480 (O–H), 1331 (SO_2), 1197 cm^{-1} (SO_2); MS *m/z* 227, 225 (M^+ − Me). Found: C, 40.18; H, 5.42%. Calcd for $C_8H_{13}ClO_4S$: C, 39.92; H, 5.44%.

Competitive Oxidation of 1c or 1d with Thioanisole by MCPBA. 14.2 mg (0.05 mmol) of **1c**, 6.2 mg (0.05 mmol) of thioanisole, and 8.6 mg (0.05 mmol) of MCPBA were dissolved in 1 mL of $CDCl_3$ in an NMR tube. The progress of the reaction was monitored by ^{1}H NMR analysis. This revealed that the oxidation (consumption of MCPBA) was completed within 4 min. This was also true for the case of **1d**. Based on the integral ratios in the ^{1}H NMR spectra, the ratios of the oxidation products were determined to be **3c**:methyl phenyl sulfoxide = 1.2:1.0 and **3d**:methyl phenyl sulfoxide = 1.1:1.0.

Conversion of the 5*H*-1,2-Oxathiole 1c to 2-(1-Adamantyl)-3-chloro-4-methylthiophene (11). A solution of 65.1 mg (0.2 mmol) of **1c** in 10 mL of toluene was heated at reflux for 24 h under argon. The reaction mixture was evaporated and the resulting faint-brown solid was chromatographed on a column of silica-gel with hexane as the eluent to give 49.2 mg (81%) of **11**: colorless crystals (from MeOH); mp 104–105 °C; ^{1}H NMR δ 1.76 (6H, br s), 2.07 (3H, br s), 2.16 (9H, br s), 6.76 (1H, s); ^{13}C NMR δ 15.14, 28.78, 36.65, 36.78, 40.88, 116.14, 120.53, 137.00, 146.68; MS *m/z* 268, 266 (M^+). Found: C, 67.59; H, 7.20%. Calcd for $C_{15}H_{19}ClS$: C, 67.52; H, 7.18%.

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12 We cannot rule out the possibility that **11** is formed through ring-opening of sulfoxide **12**.