3-Methyl-1-nonyl-2-oxocyclopentan-1-ol (2). A mixture of 3-methylcyclopentane-1,2-dione (434 mg, 3.87 mmol) and NaH (191 mg, 7.96 mmol) in ether (12 mL) was stirred at room temperature for 3 h until H_2 evolution ceased and to this solution was added a solution of nonylmagnesium bromide prepared from 1-bromononane (1.63 g, 7.87 mmol) and magnesium (230 mg, 9.47 mmol) in ether (5 mL). The refluxing mixture was stirred for 48 h, quenched with cold 10% NH_4Cl, acidified with 10% HCl, and extracted with AcOEt-hexane (1:1). The usual workup gave 785 mg (84%) of **2** as an oil, after chromatography (SiO_2, hexane-AcOEt 20:1): bp 125 °C (0.26 mm, decomposition on distillation); IR (neat) 3420 (OH), 1738 cm^{-1} (C=O); ^1H NMR δ 0.89 (br t, 3, CH_3), 1.14 (d, J = 6 Hz, 3, CH_3), 1.28 (br s, 12, CH_2), 1.40-2.40 (m, 9, CH_2, CH), 2.33 (br, 1, OH). Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 74.83; H, 11.97.

Methyl 2-Methyl-5-oxotetradecanoate (3a). A solution of **2** (410 mg, 1.71 mmol) and $LiClO_4$ (500 mg) in MeOH (20 mL) was charged in a H-type of anode compartment. To the cathode compartment was added a solution of $LiClO_4$ (250 mg) in MeOH (15 mL). The mixture was electrolyzed with platinum electrodes (1.5 × 2.0 cm^2) under a constant applied voltage of 20 V (1.8-7.7 mA/cm^2) at room temperature. After 3.6 F/mol of electricity passed, the anode solution was concentrated and the residue was taken up in AcOEt-benzene (1:1). The extracts were worked up in the usual manner and the following chromatography (SiO_2, hexane-AcOEt, 10:1) gave 425 mg (93%) of **3a**: bp 173-176 °C (0.03 mm); IR (neat) 1732 (COO), 1710 cm^{-1} (C=O); ^1H NMR δ 0.90 (br t, 3, CH_3), 1.14 (d, J = 6 Hz, 3, CH_3), 1.27 (br s, 16, CH_2), 2.10-2.67 (m, 5, CH_2CO, CHCO), 3.59 (s, 3, OCH_3). Anal. Calcd for $C_{16}H_{30}O_3$: C, 71.07; H, 11.18. Found: C, 71.15; H, 11.39.

Methyl 2-Methyl-5-methylenetetradecanoate (3b). To a solution of **3a** (278 mg, 1.03 mmol) in benzene (1 mL) was added a solution of methylenetriphenylphosphorane prepared from methyltriphenylphosphonium bromide (708 mg, 1.98 mmol) and $NaNH_2$ (238 mg, 6.1 mmol) in benzene (10 mL). The mixture was stirred at room temperature for 12 h and worked up in the usual manner to give 246 mg (89%) of **3b**, after chromatography (SiO_2, hexane-AcOEt 20:1): bp 155-157 °C (2 mm); IR (neat) 3060 (H_2C=C), 1735 (COO), 1637 cm^{-1} (C=C); ^1H NMR δ 0.91 (br t, 3, CH_3), 0.93-2.55 (m, 21, CH_2, CH), 1.14 (d, J = 6 Hz, 3, CH_3), 3.59 (s, 3, OCH_3), 4.65 (br s, 2, H_2C=C). Anal. Calcd for $C_{17}H_{32}O_2$: C, 76.06; H, 12.02. Found: C, 76.26; H, 12.20.

2-Methyl-5-methylenetetradecanoic Acid (3c). Hydrolysis of **3b** (104 mg, 0.39 mmol) in MeOH (2 mL)-KOH (105 mg, 1.81 mmol)-H_2O (0.6 mL) system was carried out at room temperature for 24 h, acidified with cold aqueous 10% HCl, and extracted with hexane-AcOEt (1:2). The usual workup gave 90 mg (91%) of **3c**.[3b]

2,5-*trans*- and 2,5-*cis*-5-(Iodomethyl)-2-methyltetradecan-5-olides (4a,b). To a solution of **3c** (62 mg, 0.244 mmol) in aqueous 0.5 N $NaHCO_3$ (1.0 mL) was added a mixture of KI (415 mg, 2.50 mmol), I_2 (190 mg, 0.75 mmol), and H_2O (0.6 mL) at 0 °C. The mixture was stirred at 15 °C for 48 h and extracted with ether. The extract was worked up in the usual manner to give 31 mg (33.6%) of **4b** (R_f 0.57, Merck PF 254, hexane-AcOEt 20:1) and 59 mg (62.3%) of **4a** (R_f 0.49). Physical constants together with elemental analyses of **4a** and **4b** are as follows. **4b**: bp 159-160 °C (0.015 mm); IR (neat) 1735 cm^{-1} (COO); ^1H NMR δ 0.89 (br t, 3, CH_3), 1.29 (br s, 12, CH_2), 1.31 (d, J = 6 Hz, 3, CH_3), 1.40-2.70 (m, 9, CH_2, CH), 3.35 (br s, 2, CH_2I); ^{13}C NMR δ 11.7 (t, CH_2I), 14.1 (q, C-14), 17.3 (q, C-2 Me), 22.6 (t, 3C), 25.0 (t), 29.2 (t), 29.4 (t), 29.5 (t), 29.6 (t), 31.8 (t), 35.1 (d), 39.9 (t), 83.7 (s, C-5), 173.7 (s, C-1). Anal. Calcd for $C_{16}H_{29}IO_2$: C, 50.53; H, 7.69. Found: C, 50.55; H, 7.77.

4a: bp 161-162 °C (0.02 mm); IR (neat) 1735 cm^{-1} (COO); ^1H NMR δ 0.88 (br t, 3, CH_3), 1.29 (br s, 12, CH_2), 1.26 (d, J = 6 Hz, 3, CH_3), 1.40-2.70 (m, 9, CH_2, CH), 3.50 (br s, 2, CH_2I); ^{13}C NMR δ 14.1 (q, C-14), 15.3 (t, CH_2I), 17.2 (q, C-2 Me), 22.7 (t), 23.3 (t), 25.4 (t), 29.2 (t), 29.4 (t), 29.5 (t), 29.7 (t), 30.6 (t), 31.9 (t), 35.1 (d, C-2), 38.7 (t), 83.3 (s, C-5), 173.7 (s, C-1). Anal. Calcd for $C_{16}H_{29}IO_2$: C, 50.53; H, 7.69. Found: C, 50.41; H, 7.98.

Benzyl 5,6-Epoxy-2-methyl-5-nonylhexanoate (5a). A solution of potassium benzyl oxide prepared from benzyl alcohol (209 mg, 1.93 mmol) and *t*-BuOK (95 mg, 0.84 mmol) in DMF (2 mL) was added to **4** (151 mg, 0.4 mmol) in DMF (0.3 mL) at 0 °C. The mixture was stirred at room temperature for 24 h, poured into cold aqueous 5% tartaric acid, and extracted. The workup gave 124 mg (86%) of **5a** after chromatography (SiO_2, hexane-AcOEt 5:1): bp 187-189 °C (0.02 mm); IR (neat) 3030, 1735 cm^{-1} (COO); ^1H NMR δ 0.88 (br t, 3, CH_3), 1.16 (d, J = 6 Hz, 3, CH_3), 1.10-1.85 (m, 20, CH_2, 1.24 (top)), 2.15-2.51 (m, 1, CHCO), 2.52 (s, 2, CH_2O), 5.10 (s, 2, CH_2OCO), 7.30 (br s, 5, PhH). Anal. Calcd for $C_{23}H_{36}O_3$: C, 76.62; H, 10.06. Found: C, 76.68; H, 10.30.

Methyl 5,6-Epoxy-2-methyl-5-nonylhexanoate (5b). To a solution of **3a** (300 mg, 1.1 mmol) in CH_2Cl_2 (3 mL) was added 80% *m*-CPBA (299 mg, 1.73 mmol) at 0 °C. The mixture was stirred at room temperature for 6 h and worked up in the usual manner to give 307 mg (98%) of **3b**: bp 120-122 °C (0.02 mm); IR (neat) 1732 cm^{-1} (COO); ^1H NMR δ 0.89 (br t, 3, CH_3), 1.10-2.80 (m, 21, CH_2, 1.27 (top)), 1.16 (d, J = 6 Hz, 3, CH_3), 2.38 (m, 1, CHCO), 2.54 (s, 2, CH_2O), 3.66 (s, 3, OCH_3). Anal. Calcd for $C_{17}H_{32}O_3$: C, 71.79; H, 11.34. Found: C, 71.73; H, 11.39.

***dl*-Malyngolide (1a) and 2-Epimalyngolide (1b).** To a solution of **5a** (55 mg, 0.15 mmol) in CH_2Cl_2 (1 mL) was added a solution of BBr_3 (153 mg, 0.61 mmol) in CH_2Cl_2 (0.3 mL) at -70 °C. The mixture was stirred at -65 ~ -60 °C for 1 h, quenched with cold water, and extracted with AcOEt. The usual workup gave 19 mg (46%) of **1b** (R_f 0.31, Merck F254, hexane-AcOEt 4:1) and 19 mg (46%) of **1a** (R_f 0.23) after chromatography (SiO_2, hexane-AcOEt 4:1). Physical constants of **1a** and **1b** together with elemental analysis **1b** are as follows. **1b**: bp 144-146 °C (0.01 mm); IR (CCl_4) 3390 (OH), 1728, 1712 cm^{-1} (COO); ^1H NMR δ 0.89 (br t, 3, CH_3), 1.26 (br s, 12, CH_2), 1.27 (d, J = 6 Hz, 3, CH_3), 1.45-2.20 (m, 8, CH_2), 2.23-2.65 (m, 1, CHCO), 2.83 (br s, 1, OH), 3.57 (br s, 2, CH_2O); ^{13}C NMR δ 14.1 (q, C-14), 17.2 (q, C-2 Me), 22.7 (t), 23.6 (t), 25.3 (t), 26.3 (t), 29.3 (t), 29.5 (t, 2C), 30.1 (t), 31.9 (t), 35.6 (d, C-2), 36.7 (t), 67.7 (t, C-5 CH_2O), 86.9 (s, C-5), 175.3 (s, C-1). Anal. Calcd for $C_{16}H_{30}O_3$: C, 71.07; H, 11.18. Found: C, 71.13; H, 11.29.

1a: bp 144-146 °C (0.01 mm); ^{13}C NMR δ 14.1 (q, C-14), 17.2 (q, C-2 Me), 22.7 (t), 23.2 (t), 25.4 (t), 27.2 (t), 29.3 (t), 29.5 (t, 2C), 30.0 (t), 31.9 (t), 35.2 (d, C-2), 37.7 (t), 67.6 (t, C-5 CH_2O), 86.4 (s, C-5), 175.5 (s, C-1).

Registry No. 1a, 74742-19-1; **1b**, 76984-84-4; **2**, 79299-93-7; **3a**, 76984-85-5; **3b**, 76917-12-9; **3c**, 74709-66-3; **4a**, 76917-13-0; **4b**, 76917-14-1; **5a**, 79299-94-8; **5b**, 79299-95-9; 3-methylcyclopentane-1,2-dione, 79299-96-0; 1-bromononane, 693-58-3.

An Efficient Synthesis of Conjugated Ketene Dithioacetals

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Ketene dithioacetals conjugated with functional groups have been exploited in a variety of synthetic applications. Conjugated olefin ketene dithioacetals have served as carbonyl umpolung reagents[1] and Diels-Alder dienes.[2] α-Oxoketene dithioacetals have been previously utilized for the synthesis of heterocyclic compounds,[3-5] Diels-Alder dienes,[6] and the indirect synthesis of α-tertiary alkyl substituted ketones.[7] The conjugated ketene dithioacetals contain a masked ester functionality and hold considerable potential as substrates for functional group manipulation and sequential carbon-carbon bond-forming transformations.

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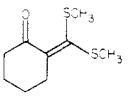
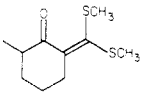
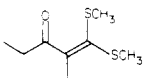
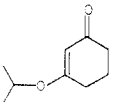
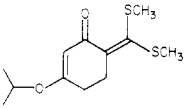
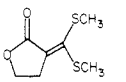
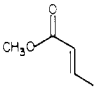
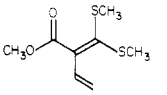
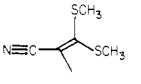
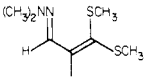
Table I. Synthesis of Conjugated Ketene Dithioacetals

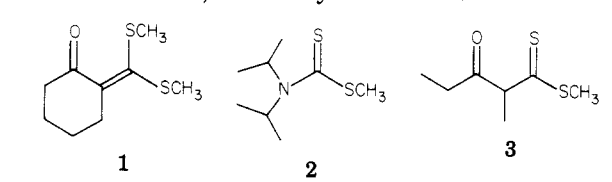
entry	substrate	procedure A,[a] % yield[c]	procedure B,[b] % yield[c]	ketene dithioacetal
1		84		 1
2			86	 6
3			81	 7
4		80		 8
5		37	81	 9
6		29	71	 10
7			83	 11
8		71[d]		 12

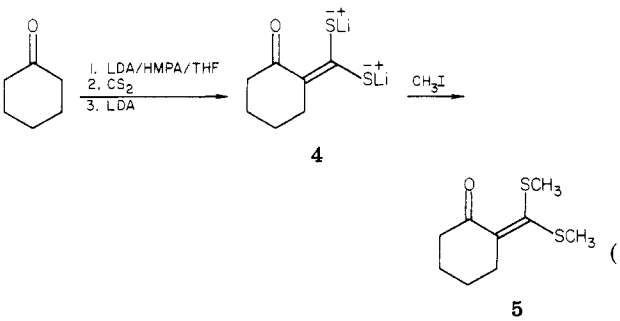
[a] Lithium diisopropylamide was employed as the base. [b] Lithium hexamethyldisilazide was employed as the base. [c] All yields are based upon isolated products purified by column chromatography on silica gel. [d] Two equivalents of HMPA per lithium atom was utilized.

As part of a program on conjugated ketene dithioacetals we have developed, and report here, an efficient method for their synthesis. The method adapts known procedures by which carbanions are generated and added to carbon disulfide in the presence of alkylating agents[7,8] and those involving alkylation of dithioic acid dianions[9] and dithio ester enolates.[10] The addition of carbon nucleophiles such as Grignard reagents,[10,11] phosphonium ylides,[12] ketone enolates,[3,7,8,13] and the conjugate bases of enaminonitriles[14] and active methylene compounds[4,15] to carbon disulfide has been reported. A general procedure, however, for the addition of kinetically generated carbon nucleophiles to carbon disulfide has not been described. A recent report[16] on the addition of lithio-1,3-dithiane to carbon disulfide prompts us to report our general synthesis of ketene dithioacetals conjugated to a variety of functional groups.

Several bases, such as sodium *tert*-amylate,[3] lithium 4-methyl-2,6-di-*tert*-butylphenoxide[7] and sodium hydride[8] have been utilized to deprotonate ketones in the presence of carbon disulfide. Simple esters, when treated with a sodium hydride/carbon disulfide/methyl iodide combination afforded primarily products resulting from Claisen condensations.[8] In an effort to obviate these difficulties and extend the useful range of carbon nucleophiles, we have examined the use of strong nonnucleophilic amide bases such as lithium diisopropylamide (LDA), lithium dicyclohexylamide (LCA), and lithium hexamethyldisilazide (LHDS).

In the initial experiment, cyclohexanone was added dropwise to 2 equiv of LDA in an HMPA/THF solvent mixture followed by sequential addition of carbon disulfide and 2 equiv of methyl iodide. Although a moderate yield of 1 was obtained, the methyl dithiocarbamate **2** was isolated as a major side product. Control experiments revealed that LDA and LCA underwent nucleophilic addition to carbon disulfide under the reaction conditions. Since competing nucleophilic addition of LDA to carbon disulfide was observed, even in the presence of HMPA, a stepwise sequential generation of the intermediate dithiolate dianion was required. Thus, the lithium enolate of cyclohexanone was generated from LDA in an HMPA/THF solvent mixture at −78 °C, quenched with carbon disulfide, and then treated with a second equivalent of LDA to yield dianion **4** (eq 1). Reaction of dianion **4**





(1)

with 2 equiv of methyl iodide afforded **5** in good yield after purification by column chromatography (petroleum ether/10% diethyl ether, v/v). As illustrated in Table I, this procedure could be extended to a variety of functional

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groups including α,β-unsaturated ketones, lactones, α,β-unsaturated esters, nitriles, and hydrazones. In one case (entry 3), the reaction was carried out in two steps and intermediate dithio ester **3** was isolated. The two-step procedure, however, offered no improvement in overall yield.

Several observations concerning the choice of base in these reactions are noteworthy. First, when 2-methylcyclohexanone was treated with 2 equiv of 4-methyl-2,6-di-*tert*-butylphenoxide[7] and 2.5 equiv of carbon disulfide in THF for 12 h and then quenched with methyl iodide, a single product was obtained which was identical in all respects (TLC, NMR, and IR) with ketene dithioacetal **6** prepared by the procedure utilizing LHDS. No methyl β-keto dithio ester resulting from addition of the more substituted enolate to carbon disulfide was observed. Second, two examples (entries 5 and 6) reveal that the reaction is sometimes sensitive to the choice of base. Here, LDA afforded low yields of conjugated ketene dithioacetals and significant amounts of condensation material. Good yields of conjugated ketene dithioacetals could be obtained from γ-butyrolactone and methyl crotonate (entries 5 and 6, respectively) when lithium hexamethyldisilazide was employed as the base.

In summary, this one-step procedure allows for the facile preparation of ketene dithioacetals conjugated to a variety of functional groups. Investigations into synthetic applications of conjugated ketene dithioacetals are in progress in our laboratory.

Experimental Section

Proton NMR spectra were recorded on either a Varian EM-360L or JEOL FX-90Q instrument. Chemical shifts are reported as δ values in parts per million relative to tetramethylsilane as internal standard. Infrared spectra were recorded on a Perkin-Elmer 710B grating spectrophotometer. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analysis were determined by Galbraith Laboratories, Inc., Knoxville, TN.

Hexamethyldisilazane was distilled and stored over 3-Å molecular sieves. Diisopropylamine was distilled over CaH_2 and stored over KOH. Tetrahydrofuran was distilled from sodium–benzophenone prior to use.

1,1-Bis(methylthio)-2-(carbomethoxy)-1,3-butadiene (10). A solution containing 50 mL of dry THF and 8.25 g (51.1 mmol) of freshly distilled hexamethyldisilazane was cooled under nitrogen to 0–5 °C, and 21.3 mL (2.3 M in hexane, 51.1 mmol) of *n*-butyllithium was added. After 15 min the solution was cooled to −78 °C and 9.13 g (51.0 mmol) of freshly distilled HMPA was added. Approximately 30 min later, 4.93 g (49.3 mmol) of methyl crotonate in 5 mL of dry THF was added dropwise over a period of 30 min. The solution was stirred at −78 °C for an additional 20 min and 3.88 g (51.0 mmol) of carbon disulfide was added in one addition. The solution immediately turned red and was allowed to warm to 0 °C over a 2-h period, whereupon the solution was cooled to −78 °C and a solution of lithium hexamethyldisilazide [prepared from 8.25 g (51.1 mmol) of hexamethyldisilazane and 21.3 mL (51.1 mmol) of *n*-butyllithium] in 50 mL of THF was added via double-tipped needle. The solution was stirred at −78 °C for 30 min upon completion of the addition and 14.48 g (102 mmol) of methyl iodide was added in one addition. The solution was allowed to warm to room temperature over a period of 1 h and then stirred at room temperature for 2 h. The dark solution was poured into saturated aqueous ammonium chloride and extracted with ether. The combined organic phase was washed with saturated aqueous ammonium chloride, water, brine, and dried over magnesium sulfate. Removal of solvent in vacuo gave 10.0 g of crude material. Purification by column chromatography (silica gel, petroleum ether/10% diethyl ether, v/v) afforded pure ketene dithioacetal **10**: 7.1 g (71% yield); IR (CCl_4) 3080 (w), 3000 (m), 2920 (s), 1740 (vs), 1605 (m), 1440 (s), 1310 (vs), 1295 (vs), 1200 (vs), 1165 (vs), 990 (s), 918 (s) cm^{-1}; NMR (CCl_4) δ 2.32 (s, 3 H), 2.35 (s, 3 H), 3.80 (s, 3 H), an ABC pattern [5.10 (dd, J_{AB} = 1 Hz, J_{AC} = 17 Hz, 1 H), 5.22 (dd, J_{BA} = 1 Hz, J_{BC} = 11 Hz, 1 H), 6.87 (dd, J_{CA} = 17 Hz, J_{CB} = 11 Hz, 1 H)].

Anal. Calcd for $C_8H_{12}O_2S_2$: C, 47.02; H, 5.93. Found: C, 47.19; H, 5.98.

Conjugated ketene dithioacetals listed in Table I were prepared according to the above procedure, utilizing either lithium diisopropylamide (procedure A) or lithium hexamethyldisilazide (procedure B) as the base. **6**: IR (CCl_4) 2985, 2940, 2875, 1700, 1380, 1320, 1135, 875, 853 cm^{-1}; NMR ($CDCl_3$) δ 1.13 (d, *J* = 6.0 Hz, 3 H), 1.24–2.22 (m, 4 H), 2.32 (s, 3 H), 2.34 (s, 3 H), 2.36–2.71 (m, 2 H), 3.02–3.36 (m, 1 H). **7**: IR (CCl_4) 2960, 2905, 1688, 1425, 1335, 1220, 1085, 1035, 890 cm^{-1}; NMR (CCl_4) δ 1.00 (t, *J* = 7.5 Hz, 3 H), 1.95 (s, 3 H), 2.15 (s, 3 H), 2.23 (s, 3 H) 2.53 (q, *J* = 7.5 Hz, 2 H). **8**: IR (CCl_4) 2970, 2920, 1630, 1605, 1385, 1300, 1200, 1115, 1010, 930 cm^{-1}; NMR ($CDCl_3$) δ 1.19 (d, *J* = 6.5 Hz, 6 H), 2.24 (s, 3 H), 2.30 (s, 3 H) 2.34 (t, *J* = 5.5 Hz, 2 H), 3.03 (t, *J* = 5.5 Hz, 2 H), 4.34 (septet, *J* = 6.5 Hz, 1 H), 5.31 (s, 1 H). Anal. Calcd for $C_{12}H_{18}O_2S_2$: C, 55.77; H, 7.04. Found: C, 55.52; H, 6.95. **9**: IR (CCl_4) 2975, 2910, 1740, 1560, 1435, 1370, 1218, 1080, 1040, 960, 900 cm^{-1}; NMR (CCl_4) δ 2.45 (s, 3 H), 2.47 (s, 3 H), 2.98 (t, *J* = 7.0 Hz, 2 H), 4.22 (t, *J* = 7.0 Hz, 2 H). Anal. Calcd for $C_7H_{10}O_2S_2$: C, 44.20; H, 5.31. Found: C, 44.05; H, 5.39. **11**: IR (CCl_4) 2925, 2200, 1540, 1430, 920 cm^{-1}; NMR (CCl_4) δ 2.05 (s, 3 H), 2.40 (s, 6 H). Anal. Calcd for $C_6H_9NS_2$: C, 45.24; H, 5.80. Found: C, 45.46; H, 5.70. **12**: IR (CCl_4) 2995, 2980, 2930, 2865, 1550, 1470, 1465, 1440, 1050, 1025, 890 cm^{-1}; NMR ($CDCl_3$) δ 2.12 (s, 3 H), 2.20 (s, 3 H), 2.27 (s, 3 H), 2.90 (s, 6 H), 7.73 (br s, 1 H). Anal. Calcd for $C_8H_{16}N_2S_2$: C, 47.02; H, 7.88. Found: C, 47.01; H, 7.91.

Methyl 2-Methyl-3-oxopentanedithioate (3). The ketone enolate of 2-pentanone (1.74 g, 20.2 mmol) was generated with lithium diisopropylamide in THF at −78 °C as described above. Carbon disulfide (1.69 g, 22.2 mmol) was added in one addition and the solution was stirred at −78 °C for 2 h. Methyl iodide (3.12 g, 22.0 mmol) was added and the solution was allowed to warm to room temperature over a period of 1 h. The solution was poured into saturated aqueous ammonium chloride and extracted with ether. The combined organic phase was washed with saturated aqueous ammonium chloride, water, brine, and dried over magnesium sulfate. Removal of solvent in vacuo gave 3.48 g of crude material. Purification by column chromatography (silica gel, petroleum ether/10% diethyl ether, v/v) afforded pure dithio ester **3**: 3.26 g (92% yield); IR (CCl_4) 2960, 2920, 1720, 1450, 1410, 1375, 1345, 1180, 960, 923 cm^{-1}; NMR (CCl_4) δ 0.97 (t, *J* = 8.0 Hz, 3 H), 1.43 (d, *J* = 7.5 Hz, 3 H), 1.87–2.67 (m, 2 H), 2.63 (s, 3 H), 4.23 (q, *J* = 7.5 Hz, 1 H).

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Secondary Metabolites from a Red Alga (*Laurencia intricata*): Sesquiterpene Alcohols[1a]

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We recently described the isolation and characterization of a new, 15-carbon nonterpenoid enyne, bermudenynol

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