Facile Reduction of Dithiocarbonates Derived from Secondary Alcohols with *n*-Bu_3SnH–Et_3B and Synthesis of 2-Furanthiones and 2-Furanones by Intramolecular Addition of Alkoxythiocarbonyl Free Radicals to Acetylenic Linkages

Kyoko Nozaki, Koichiro Oshima,* and Kiitiro Utimoto*
Department of Industrial Chemistry, Faculty of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606
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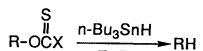
The reduction of dithiocarbonates or thiocarbonates by *n*-Bu_3SnH–Et_3B easily gives the corresponding hydrocarbons. The intermediate alkoxythiocarbonyl radical equivalents are trapped by properly located carbon–carbon multiple bonds. The dithiocarbonates derived from either homopropargylic or homoallylic alcohols produce tetrahydrofuranones upon treatment with *n*-Bu_3SnH–Et_3B. Application of this new method to the conversion of carbonyl compounds into olefins is also described.

Deoxygenation of alcohols has been one of the most important steps in organic synthesis.[1] In general, primary alcohols are easily converted into leaving groups (e.g., *p*-toluenesulfonate or methanesulfonate) and reduced either directly or via appropriate halide or sulfide. Deoxygenation of tertiary alcohols can also be readily performed by dehydration followed by hydrogenation of the resulting olefins. The major difficulty in the deoxygenation of secondary alcohols is ascribed to the fact that the carbon atoms bearing the hydroxyl groups are sterically hindered against S_N2 processes. Barton and McCombie reported the reduction of dithiocarbonates with *n*-Bu_3SnH as an effective way for deoxygenation of secondary alcohols.[2] We recently reported that Et_3B facilitated the radical addition of R_3SnH to acetylenic compounds giving vinylstannanes.[3] In the present paper, we would like to introduce the reduction of dithiocarbonates with *n*-Bu_3SnH–Et_3B as a mild and effective method for the deoxygenation of secondary alcohols. Two applications of new method are also described: (a) Conversion of carbonyl compounds into olefins via dithiocarbonates of β-phenylthio alcohols, and (b) Synthesis of tetrahydrofuranthiones by treatment of dithiocarbonates having properly located triple or double bonds with *n*-Bu_3SnH–Et_3B by intramolecular addition of the intermediate free radicals.[4]

(1) Reduction of Dithiocarbonate with *n*-Bu_3SnH–Et_3B. Treatment of dithiocarbonate **1a** (1.0 mmol) with *n*-Bu_3SnH[5] (1.1 mmol) and Et_3B[6] (1.1 mmol) in benzene at 20 °C gave the deoxygenated product **2a** in 93% yield. The reduction of dithiocarbonates (**1a**, **1b**, and **1c**) or thiocarbonates[7] (**1e** and **1f**) derived from secondary alcohols proceeded smoothly to give the corresponding hydrocarbons under milder conditions (20 °C, 20 min) than those normally employed (with AIBN in refluxing toluene).[2] Meanwhile, dithiocarbonates generated from primary alcohols did not give good results. For instance, the reaction of dithiocarbonate **1d** afforded tetradecane in 18% yield along with 1-tetradecanol (30%).[8]



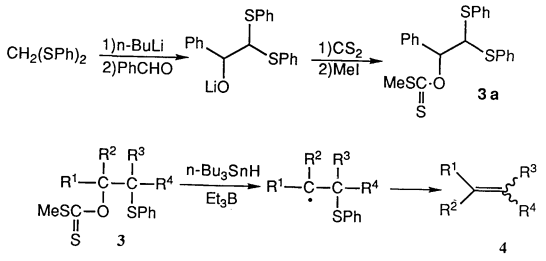
1a: R = cyclododecyl; X = SMe (93%)
1b: R = diphenylmethyl; X = SMe (88%)
1c: R = 1-hexylheptyl; X = SMe (83%)
1d: R = tetradecyl; X = SMe (18%)
1e: R = cyclododecyl; X = OPh (82%)
1f: R = PhCH(COOEt); X = OPh (78 %)

Scheme 1.

(2) Synthesis of Olefins from Carbonyl Compounds. The applicability of this reaction to the synthesis of olefins from carbonyl compounds has been examined.[9,10] Dithiocarbonates of β-phenylthio alcohols were prepared by the reaction of α-lithiothioacetals or α-lithiosulfides with aldehydes followed by treatment with carbon disulfide and methyl iodide. For example, the preparation of *O*-[2,2-bis(phenylthio)-1-phenylethyl] *S*-methyl dithiocarbonate (**3a**) is described in Scheme 2.

Treatment of these *O*-(2-phenylthioalkyl) dithiocarbonates with *n*-Bu_3SnH–Et_3B afforded the corresponding olefins with the elimination of phenylthio radical from intermediary occurring 2-phenylthioalkyl radicals (Scheme 2).

Tributylstannane (1.1 mmol) was added dropwise to a solution of Et_3B (1.1 mmol) and dithiocarbonate **3a** (1.0 mmol) in benzene (3.0 ml) at 20 °C under an argon



Scheme 2.

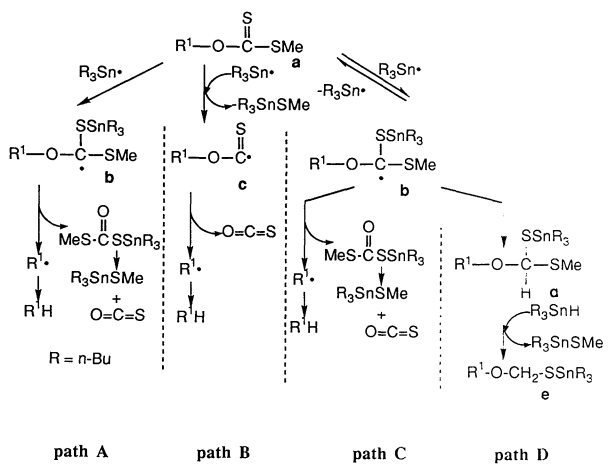
Table 1. Synthesis of Olefins from Dithiocarbonates by Reduction with n-Bu_3SnH–Et_3B

Entry		Dithiocarbonate **3**				Yield (%)	Product **4**
		R^1	R^2	R^3	R^4		E/Z
1	**3a**	Ph	H	PhS	H	70	92/8
2	**3b**	n-C_6H_{13}	H	PhS	H	75	50/50
3	**3c**	Ph	H	PhS	Me	100	63/37[a]
4	**3d**	Ph	H	Ph	H	80	100/0
5	**3e**	n-C_8H_{17}	H	Ph	H	71	100/0
6	**3f**	Ph	H	n-C_8H_{17}	H	41	100/0

a) The major product was tentatively assigned as E-isomer.

atmosphere. The resulting mixture was stirred for 15 min at 20 °C to give β-phenylthiostyrene **4a** in 70% yield. The results are summarized in Table 1.

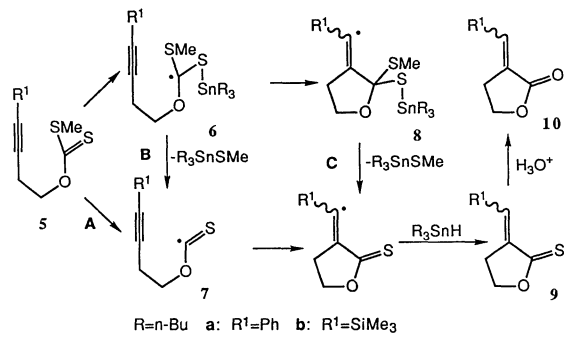
(3) Synthesis of 2-Furanthiones and 2-Furanones by Intramolecular Addition of Intermediary Radicals in the Barton Reduction. Two mechanistic pathway have been proposed for the deoxygenation process by Barton[1a,2] and Beckwith.[11] The first explanation by Barton is outlined in Scheme 3, path **A**.[2] Tributylstannyl radical attacks the thiocarbonyl sulfur of the dithiocarbonate **a** to produce a radical intermediate **b** which undergoes β-scission to thiocarbonate and an alkyl radical ($R^1\cdot$). Hydrogen abstraction from the stannane gives the alkane (R^1H) and regenerates tributylstannyl radical thus completing the cycle of this chain reaction. Beckwith proposed the second mechanism involving a direct S_H2 attack of the stannyl radical on the sulfur (SMe, Scheme 3, path **B**).[11] This leads to an alkoxythiocarbonyl radical **c** which looses a molecule of carbonyl sulfide to give an alkyl radical. The existence of alkoxythiocarbonyl radical **c** was confirmed by the observation of its e.p.r. signal. Recently, Barton and Beckwith have agreed with the mechanism described in path **C**, in which the addition of tributylstannyl radical is considered reversible and the fragmentation of radical **b** is the rate determining step. Path **D** shows a reduction of radical **b** by n-Bu_3SnH before the desired fragmentation. This path



Scheme 3.

D explains our result in the reduction of dithiocarbonate derived from primary alcohol (Scheme 1, **1d**). In this case, the fragmentation was so slow that the reduced compound **e** was the major product to give the original alcohol after aqueous work-up.

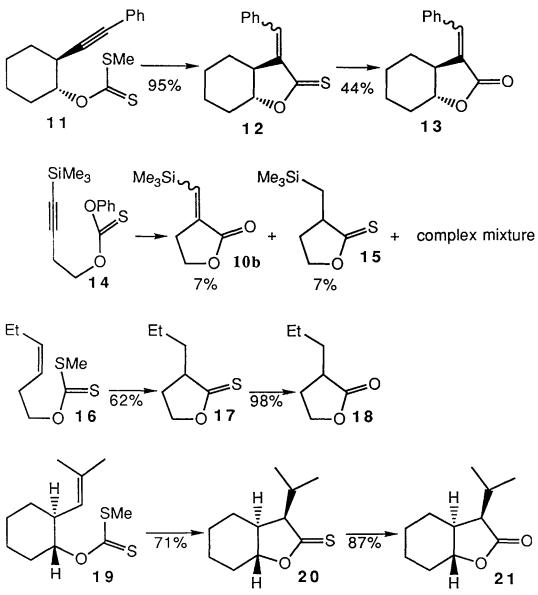
Irrespective of the precise mechanism of the reaction, trapping the intermediate **b** or **c** by an intramolecular multiple bond would offer promising possibilities for tetrahydrofuranthione synthesis. Thus, we prepared two dithiocarbonates having properly located carbon–carbon triple bonds and examined their behavior toward n-Bu_3SnH–Et_3B system (Scheme 4).[12,13]



Scheme 4.

Treatment of dithiocarbonate **5a** (1.0 mmol) with n-Bu_3SnH (1.1 mmol) and Et_3B (1.1 mmol) at −78 °C afforded 3-benzylidene-4,5-dihydro-2(3*H*)-furanthione **9a** in 53% yield. The product was not contaminated by benzyldihydro-2(3*H*)-furanthione (<1%), which is generated by reduction of initially formed **9a** with n-Bu_3SnH under ordinary reaction conditions (with AIBN in refluxing benzene).[14] Reduction of **5b** provided the corresponding tetrahydrofuranthione **9b** in 66% yield in a similar fashion. The reaction could proceed by the intramolecular cyclization of the intermediary radical **6** or **7**. Generality and mildness of the reaction which employs readily available starting materials are shown by the following examples.

Dithiocarbonate **11** derived from secondary alcohol also provided the desired tetrahydrofuranthione **12** in good yield in preference to deoxygenation to hydro-



carbon. The extension of this method to the preparation of lactone **10b** from thiocarbonate **14** resulted in low yield. Tetrahydrofuranthiones were also produced from dithiocarbonates derived from homoallylic alcohols (**16** to **17**, **19** to **20**). The resulting tetrahydrofuranthiones were easily converted into the corresponding lactones under acidic conditions. Compound **20** and **21** were single diastereomers by examination of ^{1}H NMR and ^{13}C NMR. The stereochemistry was determined by the following reasons. 1) No epimerization was observed when the lactone **21** was treated with DABCO (1,4-diazabicyclo[2.2.2]octane). This result may suggest that the isopropyl group occupies thermodynamically more stable position. 2) Beckwith[15] and Houk[16] have reported theoretical studies on stereoselectivity of radical ring closure. These studies aniticipate that isopropyl group would be trans to the substrate on 3a-carbon.

Experimental

Distillation of the products was performed by the use of Kugelrohr (Büchi), and boiling points are indicated by an air bath temperature without correction. All melting points were obtained on Yanaco MP-50929 melting points apparatus and are uncorrected. The IR spectra were determined on a JASCO IR-810 spectrometer, the mass spectra on a Hitachi M-80 machine, the ^{1}H and ^{13}C NMR spectra on Varian XL-200 spectrometers. The chemical shifts of the ^{1}H NMR are given in δ with Me_4Si as an internal standard, and those of the ^{13}C NMR are given in δ with $CDCl_3$. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyls. Purification of products was performed by column chromatography or preparative thin-layer chromatography (TLC) on silica gel.

Preparation of Dithiocarbonates from Alcohols. Dithiocarbonates were prepared according to the procedure described in Ref. 1a. To a dispersion of sodium hydride (80 mg, 60 wt% in oil, 2.0 mmol) in 3 ml of THF, was slowly added a THF solution of cyclododecanol (1.0 M, 1 M=1 mol dm^{-3}, 2.0 ml, 2.0 mmol) at 0 °C under an argon atmosphere. After 15 min at 20 °C, carbon disulfide (0.13 ml, 2.2 mmol) was added. The resulting brown solution was stirred for 1 h at 20 °C. To this mixture was added methyl iodide (0.15 ml, 2.4 mmol) and the color of the solution turned yellow. After 1 h at 20 °C, the reaction mixture was poured into water. The organic layer was washed with brine and the aqueous layers were extracted by ethyl acetate three times. The combined organic layers were evaporated and purified by column chromatography on silica gel affording 0.24 g of *O*-cyclododecyl *S*-methyl dithiocarbonate (**1a**) in 88% yield: mp 46 °C (methanol); IR (KBr) 2924, 2848, 1470, 1447, 1248, 1214, 1194, 1172, 1148, 1064, 1021, 967 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.26—1.65 (m, 18H), 1.65—2.00 (m, 4H), 2.57 (s, 3H), 5.83—5.98 (m, 1H). Found: C, 61.50; H, 9.78%. Calcd for $C_{14}H_{26}OS_2$: C, 61.26; H, 9.55%.

***O*-Diphenylmethyl *S*-Methyl Dithiocarbonate (1b):** 77% yield; mp 66.5 °C (methanol); IR (KBr) 3062, 3026, 1635, 1490, 1450, 872, 827, 740, 695, 627 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.40 (s, 3H), 6.09 (s, 1H), 7.20—7.45 (m, 10H). Found: C, 65.41; H, 5.01%. Calcd for $C_{15}H_{14}OS_2$: C, 65.66; H, 5.14%.

***O*-(1-Hexylheptyl) *S*-Methyl Dithiocarbonate (1c):** 71% yield; bp 128 °C (bath temp, 1.0 Torr, 1 Torr=133.322 Pa); IR (neat) 2922, 2854, 1461, 1427, 1378, 1318, 1214, 1120, 1045 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=7.0 Hz, 6H), 1.28 (bs, 16H), 1.55—1.85 (m, 4H), 2.55 (s, 3H), 5.65—5.80 (m, 1H). Found: C, 62.15; H, 10.67%. Calcd for $C_{15}H_{30}OS_2$: C, 62.01; H, 10.41%.

***S*-Methyl *O*-Tetradecyl Dithiocarbonate (1d):** 91% yield; bp 132 °C (bath temp, 1.0 Torr); IR (neat) 2920, 2850, 1466, 1222, 1063 cm^{-1}; ^{1}H NMR δ=0.90 (t, J=7.0 Hz, 3H), 1.26 (bs, 24H), 2.56 (s, 3H), 4.62 (t, J=7.0 Hz, 2H). Found: C, 63.18; H, 10.77%. Calcd for $C_{16}H_{32}OS_2$: C, 63.10; H, 10.59%.

Preparation of Thiocarbonates. *O*-Phenyl chlorothioformate (0.35 g, 2.0 mmol) was added slowly to a mixture of cyclododecanol (0.37 g, 2.0 mmol) and pyridine (0.17 g, 2.2 mmol) in THF (8 ml) at 0 °C under an argon atmosphere. After 15 min at 0 °C, the ice bath was removed. After stirring for further 1 h at 20 °C, the reaction mixture was poured into water. The organic layer was washed with brine and the aqueous layers were extracted by ethyl acetate three times. Purification by silica-gel column chromatography gave 0.27 g of *O*-cyclododecyl *O*-phenyl thiocarbonate (**1e**) in 84% yield: mp 59.7 °C (methanol); IR (KBr) 2848, 1590, 1489, 1467, 1147, 991, 767 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.25—1.65 (m, 18H), 1.65—2.00 (m, 4H), 5.47—5.63 (m, 1H), 7.10—7.57 (m, 5H). Found: C, 71.14; H, 8.80%. Calcd for $C_{19}H_{28}O_2S$: C, 71.21; H, 8.81%.

***O*-(α-Ethoxycarbonylbenzyl) *O*-Phenyl Thiocarbonate (1f):** 82% yield; mp 57.5 °C (hexane); IR (KBr) 2976, 1751, 1591, 1490, 1457, 1269, 1225, 1198, 1052, 1016, 754, 686 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.25 (t, J=7.2 Hz, 3H), 4.13—4.40 (m, 2H), 6.37 (s, 1H), 7.13—7.65 (m, 10H). Found: C, 64.70; H, 5.08%. Calcd for $C_{17}H_{16}O_4S$: C, 64.54; H, 5.10%.

Deoxygenation of Dithiocarbonates or Thiocarbonates. Typical procedure is as follows. To a mixture of dithiocarbonate **1a** (0.27 g, 1.0 mmol) and *n*-Bu_3SnH (0.32 g, 1.1 mmol) in benzene (3.0 ml) was added a hexane solution of Et_3B (1.0 M, 1.1 ml, 1.1 mmol) at 20 °C under an argon

atmosphere. After stirring for 20 min, potassium fluoride[17] (200 mg) and water (2 ml) were added. The heterogeneous mixture was stirred vigorously and the precipitated solids were removed by filtration. The organic layer was separated and the aqueous layer was extracted by ethyl acetate twice. The combined organic layers were concentrated and purified by column chromatography on silica gel to give 0.16 g of cyclododecane in 93% yield. Other results are summarized in Scheme 1.

Preparation of *S*-Methyl *O*-(2-Phenylthioalkyl) Dithiocarbonates from Thioacetals or Sulfides and Aldehydes. The representative procedure is as follows. A hexane solution of butyllithium (1.56 M, 1.3 ml, 2.0 mmol) was added to a THF solution of bis(phenylthio)methane (0.50 M, 4.0 ml, 2.0 mmol) at −40 °C under an argon atmosphere. After 20 min at −40 °C, benzaldehyde (0.21 g, 2.0 mmol) was added to this yellow mixture, then the resulting solution was warmed up to 0 °C and stirred for another 20 min. HMPA (0.5 ml) and carbon disulfide (0.13 ml, 2.2 mmol) were added. After stirring for 1 h at 20 °C, methyl iodide (0.15 ml, 2.4 mmol) was added to this brown solution and the solution turned yellow. This mixture was allowed to stand at 20 °C for 1 h and poured into water. The organic layer was washed with brine and the aqueous layers were extracted by ethyl acetate three times. The organic layer were evaporated and purified by silica-gel column chromatography to give 0.34 g of *O*-[2,2-bis(phenylthio)-1-phenylethyl] *S*-methyl dithiocarbonate (**3a**) in 80% yield: decomposes above 100 °C; IR (neat) 3054, 2930, 1644, 1582, 1451, 1439, 1024, 867 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.31 (s, 3H), 4.74 (d, J=4.7 Hz, 1H), 5.21 (d, J=4.7 Hz, 1H), 7.25—7.65 (m, 15H). Found: C, 61.36; H, 4.81%. Calcd for $C_{22}H_{20}OS_4$: C, 61.64; H, 4.70%

***O*-[1,1-Bis(phenylthio)methylheptyl] *S*-Methyl Dithiocarbonate (3b):** 71% yield; pale yellow oil which decomposes above 120 °C; IR (neat) 2922, 2852, 1479, 1439, 1208, 1056, 733, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, J=7.5 Hz, 3H), 1.26 (bs, 12H), 1.97—2.15 (m, 2H), 2.50 (s, 3H), 4.81 (d, J=3.5 Hz, 1H), 5.88—6.00 (m, 1H), 7.10—7.50 (m, 10H). Found: C, 62.26; H, 7.03%. Calcd for $C_{24}H_{32}OS_4$: C, 62.02; H, 6.94%

***O*-[2,2-Bis(phenylthio)-1-phenylpropyl] *S*-Methyl Dithiocarbonate (3c):** 46% yield; mp 94.2 °C (methanol); IR (KBr) 1590, 1440, 1226, 1194, 1060, 751, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.11 (s, 3H), 2.62 (s, 3H), 6.62 (s, 1H), 7.10—7.70 (m, 15H). Found: C, 62.57; H, 4.96%. Calcd for $C_{23}H_{22}OS_4$: C, 62.41; H, 5.01%.

***S*-Methyl *O*-(1,2-Diphenyl-2-phenylthioethyl) Dithiocarbonate (3d, 77/23 diastereomeric mixture):** 61% yield; mp 133 °C (methanol); IR (KBr) 3070, 3024, 1635, 1454, 1198, 1057, 877, 864, 694 cm^{-1}; ^1H NMR ($CDCl_3$) for major, δ=2.33 (s, 3H), 4.60 (d, J=7.9 Hz, 1H), 5.26 (d, J=7.9 Hz, 1H), 7.00—7.40 (m, 15H); for minor, δ=2.33 (s, 3H), 4.76 (d, J=8.1 Hz, 1H), 6.92 (d, J=8.1 Hz, 1H), 7.00—7.40 (m, 15H). Found C, 66.36; H, 4.98%. Calcd for $C_{22}H_{20}OS_3$: C, 66.63; H, 5.08%.

***S*-Methyl *O*-[1-(α-Phenylthiobenzyl)nonyl] Dithiocarbonate (3e, 78/22 diastereomeric mixture):** Decomposes above 150 °C, IR (neat) 3056, 3022, 2922, 2848, 1710, 1654, 1439, 963, 880, 829, 740, 687 cm^{-1}; ^1H NMR ($CDCl_3$) for major, δ=0.86 (t, J=6.5 Hz, 3H), 1.20 (bs, 12H), 1.50—2.00 (m, 2H), 2.51 (s, 3H), 4.62 (d, J=6.3 Hz, 1H), 6.05—6.20 (m, 1H), 7.15—7.52 (m, 10H); for minor, δ=0.86 (t, J=6.5 Hz, 3H), 1.20 (bs, 12H), 1.50—2.00 (m, 2H), 2.50 (s, 3H), 4.67 (d, J=5.0 Hz, 1H), 6.05—6.20 (m, 1H), 7.15—7.52 (m, 10H). Found: C, 66.37; H, 7.27%. Calcd for $C_{24}H_{32}OS_3$: C, 66.62; H, 7.45%.

***S*-Methyl *O*-(1-Phenyl-2-phenylthiodecyl) Dithiocarbonate (3f):** Decomposes above 150 °C; IR (neat) 3056, 3026, 2922, 2850, 1646, 1452, 867, 742, 697 cm^{-1}; ^1H NMR ($CDCl_3$) for major, δ=0.87 (t, J=6.6 Hz, 3H), 1.22 (bs, 12H), 1.35—1.85 (m, 2H), 2.38 (s, 3H), 3.40—3.55 (m, 1H), 5.06 (d, J=5.4 Hz, 1H), 7.15—7.42 (m, 10H); for minor, δ=0.87 (t, J=6.6 Hz, 3H), 1.22 (bs, 12H), 1.35—1.85 (m, 2H), 2.37 (s, 3H), 3.40—3.55 (m, 1H), 5.07 (d, J=6.0 Hz, 1H), 7.15—7.42 (m, 10H). Found: C, 66.87; H, 7.51%. Calcd for $C_{24}H_{32}OS_3$: C, 66.62; H, 7.45%.

Reaction of *S*-Methylthio *O*-(2-Phenylthioalkyl) Dithiocarbonates with n-Bu_3SnH–Et_3B System. The representative procedure is as follows. A benzene solution of n-Bu_3SnH (0.5 M, 2.2 ml, 1.1 mmol) was added dropwise to a mixture of dithiocarbonate **3a** (0.43 g, 0.5 mmol) and Et_3B (1.0 M in hexane, 1.1 ml, 1.1 mmol) in benzene (3.0 ml) at 20 °C under an argon atmosphere. The resulting mixture was stirred for 15 min at 20 °C. Treatment with potassium fluoride and extractive workup followed by purification by preparative tlc on silica gel gave β-phenylthiostyrene **4a** (0.15 g) in 70% yield.

Preparation of Dithiocarbonates Derived from β,γ-Unsaturated Alcohols. The preparation of *S*-methyl *O*-(4-phenyl-3-butynyl) dithiocarbonate (**5a**) is representative. 4-Phenyl-3-butyn-1-ol (0.29 g, 2.0 mmol) was treated with sodium hydride (2.0 mmol), carbon disulfide (2.2 mmol), and methyl iodide (2.4 mmol) according to the procedure for the preparation of **1a** producing 0.23 g of **5a** in 49% yield: bp 97.0 °C (bath temp, 1.0 Torr); IR (neat) 2910, 1489, 1221, 1079, 970, 755, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.59 (s, 3H), 2.93 (t, J=7.0 Hz, 2H), 4.78 (t, J=7.0 Hz, 2H), 7.25—7.50 (m, 5H). Found: C, 60.97; H, 5.05%. Calcd for $C_{12}H_{12}OS_2$: C, 60.98; H, 5.12%.

***S*-Methyl *O*-(4-Trimethylsilyl-3-butynyl) Dithiocarbonate (5b):** 4-Trimethylsilyl-3-butyn-1-ol gave **5b** in 78% yield: bp 85.0 °C (bath temp, 1.0 Torr); IR (neat) 2954, 2180, 1249, 1219, 1177, 1079, 843, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.54 (s, 9H), 2.58 (s, 3H), 2.78 (t, J=7.0 Hz, 2H), 4.71 (t, J=7.0 Hz, 2H). Found: C, 46.36; H, 7.02%. Calcd for $C_9H_{16}OS_2Si$: C, 46.51; H, 6.94%.

***S*-Methyl *O*-*trans*-2-Phenylethynylcyclohexyl Dithiocarbonate (11):** 2-(Phenylethynyl)cyclohexanol[18] gave **11** in 68% yield; mp 61.2 °C (methanol); IR (neat, before crystallization) 2926, 2858, 1487, 1440, 1253, 1225, 1055, 1037, 969, 760, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.25—2.40 (m, 8H), 2.58 (s, 3H), 2.93—3.08 (m, 2H), 5.65—5.80 (m, 2H), 7.25—7.50 (m, 5H). Found: C, 66.47; H, 6.23%. Calcd for $C_{16}H_{20}OS_2$: C, 66.17; H, 6.25%.

***O*-Phenyl *O*-(4-Trimethylsilyl-3-butynyl) Thiocarbonate (14):** 4-Trimethylsilyl-3-butyn-1-ol was treated with *O*-phenyl chlorothioformate and pyridine according to the preparation of **1e**. The desired thiocarbonate **14** was obtained in 67% yield. bp 83 °C (bath temp, 1.0 Torr); IR (neat) 2956, 2180, 1591, 1490, 1386, 1277, 1250, 1203, 1022, 908, 844, 769, 732, 687 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.18 (s, 9H), 2.80 (t, J=7.5 Hz, 2H), 4.64 (t, J=7.5 Hz, 2H), 7.10—7.53 (m, 5H). Found: C, 59.82; H, 6.78%. Calcd for $C_{14}H_{18}O_2SSi$: C, 60.39; H, 6.52%.

***O*-[(*Z*)-3-Hexenyl] *S*-Methyl Dithiocarbonate (16):** 80%

yield; bp 67 °C (bath temp, 1.0 Torr) IR (neat) 3006, 2960, 2920, 2870, 1459, 1424, 1218, 1183, 1133, 1070, 965, 726 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.00 (t, J=7.0 Hz, 3H), 2.00—2.20 (m, 2H), 2.50—2.65 (m, 2H), 2.56 (s, 3H), 4.61 (t, J=7.0 Hz, 2H), 5.30—5.66 (m, 2H). Found: C, 50.52; H, 7.69 %. Calcd for $C_8H_{14}OS_2$: C, 50.49; H, 7.41%.

Cyclization of Dithiocarbonates Derived from Homopropargyl Alcohols. A toluene solution of tributylstannane (0.50 M, 1.1 ml, 0.55 mmol) was added slowly to a mixture of *S*-methyl *O*-(4-phenyl-3-butynyl) dithiocarbonate (**5a**) (0.12 g, 0.50 mmol) and triethylborane (1.0 M in hexane, 0.50 ml, 0.50 mmol) in toluene (2.0 ml) at −78 °C under an argon atmosphere. After stirring for 30 min at −78 °C, treatment with potassium fluoride and extractive work-up followed by purification by silica-gel column chromatography gave 50 mg of 4,5-dihydro-3-(*E*)-benzylidene-2(3*H*)-furanthione (**9a**) as a single product in 53% yield: mp 132.8 °C (hexane), R_f=0.31 (hexane/ethyl acetate=3/1); IR (neat, before crystallization) 2960, 2916, 2856, 1735, 1637, 1467, 1444, 1389, 1276, 1256, 1220, 1172, 1151, 1078, 931, 764, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.33 (dt, J=2.8, 7.6 Hz, 2H), 4.73 (t, J=7.6 Hz, 2H), 7.45—7.55 (m, 3H), 7.55—7.67 (m, 2H), 7.94 (t, J=2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=28.55, 73.01, 128.96, 130.07, 130.28, 134.98, 135.46, 139.62 (Thiocarbonyl carbon was not observed.). Found: C, 69.15; H, 5.24%. Calcd for $C_{11}H_{10}OS$: C, 69.44; H, 5.30%.

4,5-Dihydro-3-(trimethylsilylmethylene)-2(3*H*)-furanthione (9b). Instead of potassium fluoride, aqueous hydrochloric acid (1.0 M) was used for work-up (Treatment with potassium fluoride caused desilylation and decomposition of the desired product.). **9b**: 66% yield; bp 150 °C (bath temp, 20 Torr); R_f=0.27 (hexane/ethyl acetate=5/1); IR (neat, the mixture of E/Z=83/17) 2955, 2920, 2870, 2847, 1726, 1373, 1312, 1240, 1160, 860, 840 cm^{-1}; ^1H NMR (*E*-isomer, $CDCl_3$) δ=0.18 (s, 9H), 3.02 (dt, J=2.7, 7.5 Hz, 2H), 4.61 (t, J=7.5 Hz, 2H), 7.24 (t, J=2.7 Hz, 1H); (*Z*-isomer, $CDCl_3$) δ=0.27 (s, 9H), 3.08 (dt, J=2.4, 7.7 Hz, 2H), 4.57 (t, J=7.7 Hz, 2H), 6.35 (t, J=2.4 Hz, 1H); ^{13}C NMR (*E*-isomer, $CDCl_3$) δ=−1.42, 28.15, 72.49, 141.64 (Two of the sp^2 carbons were not observed.). Found: m/z 186.0570. Calcd for $C_8H_{14}OSSi$: M, 186.0534.

***trans*-Hexahydro-3-benzylidene-2(3*H*)-benzofuranthione (12):** 61% yield (*E*/*Z*=83/17); orange oil; R_f=0.44 (hexane/ethyl acetate=5/1); IR (neat, the mixture of *E*/*Z*=83/17) 2930, 2855, 1725, 1640, 1444, 1260, 1173, 1120, 1095, 1030, 982 cm^{-1}: ^1H NMR (*E*-isomer, $CDCl_3$) δ=0.85—2.10 (m, 6H), 2.15—2.50 (m, 2H), 2.76 (dddd, J=3.0, 3.0, 11.0, 11.0 Hz, 1H), 3.95 (ddd, J=3.6, 11.0, 11.0 Hz, 1H), 7.40 (bs, 5H), 7.95 (d, J=3.0 Hz, 1H); (*Z*-isomer, $CDCl_3$) δ=0.85—2.50 (m, 8H), 2.65 (dddd, J=3.0, 3.0, 11.0, 11.0 Hz, 1H), 4.11 (ddd, J=3.6, 11.0, 11.0 Hz, 1H), 6.78 (d, J=3.0 Hz, 1H), 7.35—7.50 (m, 3H), 7.65—7.73 (m, 2H); ^{13}C NMR (*E*-isomer, $CDCl_3$) δ=24.13, 25.35, 26.56, 30.44, 48.21, 90.16, 128.04, 129.03, 129.64, 138.67, 141.21 (Two of the sp^2 carbons were not observed.).

Cyclization of Dithiocarbonates Derived from Homoallyl Alcohols. A toluene solution of tributylstannane (0.50 M, 1.1 ml, 0.55 mmol) was added slowly to a mixture of *O*-[(*Z*)-3-hexenyl] *S*-methyldithiocarbonate (**16**) (95 mg, 0.50 mmol) and triethylborane (1.0 M in hexane, 0.50 ml, 0.50 mmol) in toluene (2.0 ml) at 0 °C under an argon atmosphere. After stirring for 15 min at 0 °C, treatment with potassium fluoride and extractive work-up followed by purification by silica-gel column chromatography gave 43 mg of 4,5-dihydro-3-propyl-2(3*H*)-furanthione (**17**) as a single product in 62% yield: bp 132 °C (bath temp, 760 Torr); R_f=0.30 (hexane/ethyl acetate=5/1); IR (neat) 2958, 2932, 2870, 1466, 1455, 1373, 1304, 1264, 1240, 1206, 1167, 1121, 997, 921, 888 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.98 (t, J=6.9 Hz, 3H), 1.30—1.60 (m, 3H), 1.93 (dddd, J=8.5, 9.5, 12.0, 22.0 Hz, 1H), 2.13—2.28 (m, 1H), 4.46 (dddd, J=3.5, 6.8, 8.4, 12.0 Hz, 1H), 2.78 (m, 1H), 4.51 (ddd, J=6.8, 9.3, 9.5 Hz, 1H), 4.67 (ddd, J=3.5, 8.5, 9.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=13.79, 20.63, 29.49, 35.74, 53.53, 74.61 (Thiocarbonyl carbon was not observed.). Found: C, 58.02; H, 8.33%. Calcd for $C_7H_{12}OS$: C, 58.29; H, 8.39%.

***rel*-(3*R*,3a*S*,7a*R*)-3a,4,5,6,7,7a-Hexahydro-3-isopropyl-2(3*H*)-benzofuranthione (20):** 71% yield; bp 150 °C (bath temp, 1.0 Torr); R_f=0.60 (hexane/ethyl acetate=5/1); IR (neat) 2934, 2866, 1727, 1466, 1448, 1314, 1298, 1263, 1240, 1171, 1081, 967, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.92 (d, J=6.8 Hz, 3H), 1.11 (d, J=7.2 Hz, 3H), 1.25—1.90 (m, 6H), 1.90—2.05 (m, 1H), 2.06—2.25 (m, 1H), 2.30—2.47 (m, 1H), 2.30—2.47 (m, 1H), 2.40 (dd, J=12.5, 2.6 Hz, 1H), 2.72 (dqq, J=2.6, 6.8, 7.2 Hz, 1H), 3.95 (ddd, J=3.8, 10.8, 11.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=17.10, 21.71, 23.89, 25.18, 28.94, 30.03, 45.29, 64.20, 88.98 (Thiocarbonyl carbon was not observed.). Found: m/z 198.1059. Calcd for $C_{11}H_{18}OS$: M, 198.1077.

Hydrolysis of Tetrahydrofuranthiones into Lactones. Tetrahydrofuranthione **9a** (30 mg, 0.16 mmol) was treated with concentrated aqueous hydrochloric acid (1.0 ml)-ethanol (1.0 ml) overnight at room temperature to give (*E*)-4,5-dihydro-3-benzylidene-2(3*H*)-furanone (**10a**, 26 mg)[19] in 92% yield: ^1H NMR ($CDCl_3$) δ=3.27 (dt, J=2.9, 7.3 Hz, 2H), 4.49 (t, J=7.3 Hz, 2H), 7.40— 7.62 (m, 5H), 7.60 (t, J=2.9 Hz, 1H).

4,5-Dihydro-3-trimethylsilylmethylene-2(3*H*)-furanone (10b): 41% yield; bp 130 °C (bath temp, 20 Torr); IR (neat) 2956, 2926, 1758, 1252, 1175, 1037, 1021, 865, 841 cm^{-1}; ^1H NMR δ=0.17 (s, 9H), 2.94 (dt, J=2.9, 7.4 Hz, 2H), 4.36 (t, J=7.4 Hz, 2H), 6.93 (t, J=2.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=−1.42, 27.28, 64.98, 138.76, 139.61 (Carbonyl carbon was not observed.). Found: m/z 169.0700. Calcd for $C_8H_{13}O_2Si$: M−1, 169.0684.

***trans*-Hexahydro-3-benzylidene-2(3*H*)-benzofuranone (13)[20]:** 44% yield (*E*/*Z*=83/17); yellow oil; R_f=0.34 (hexane/ethyl acetate=5/1); IR (neat) 2932, 2860, 1757, 1656, 1448, 1227, 1188, 1130, 1015, 765, 703 cm^{-1}; ^1H NMR (*E*-isomer, $CDCl_3$) δ=0.90—2.10 (m, 6H), 2.17—2.42 (m, 2H), 2.73 (dddd, J=3.0, 3.1, 11.0, 11.5 Hz, 1H), 3.76 (ddd, J=3.5, 10.6, 11.5 Hz, 1H), 7.30—7.52 (m, 5H), 7.63 (d, J=3.1 Hz, 1H); (*Z*-isomer, $CDCl_3$) δ=0.90—2.42 (m, 8H), 2.62 (dddd, J=3.0, 3.0, 11.0, 11.0 Hz, 1H), 3.80 (ddd, J=3.0, 3.0, 11.0 Hz, 1H), 6.66 (d, J=3.0 Hz, 1H), 7.30—7.52 (m, 3H), 7.85—7.95 (m, 2H); ^{13}C NMR (*E*-isomer, $CDCl_3$) δ=24.06, 25.50, 26.43, 30.52, 48.20, 83.54, 128.10, 128.88, 129.38, 134.01, 135.98 (Two of the sp^2 carbons were not observed.).

4,5-Dihydro-3-propyl-2(3*H*)-furanone (18): 98% yield; IR (neat) 2956, 2928, 2870, 1764, 1466, 1459, 1376, 1215, 1169, 1130, 1024 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.96 (t, J=6.7 Hz, 3H), 1.33—1.60 (m, 3H), 1.75—2.10 (m, 2H), 2.33—2.70 (m, 2H), 4.20 (ddd, J=6.6, 9.0, 9.0 Hz, 1H), 4.35 (ddd, J=3.1, 9.0, 9.0 Hz, 1H); Found: m/z 128.0776, 127.0796. Calcd for $C_7H_{12}O_2$: M, 128.0836. $C_7H_{11}O_2$: M−1, 127.0758.

***rel*-(3*R*,3a*S*,7a*R*)-3a,4,5,6,7,7a-Hexahydro-3-isopropyl-2-(3*H*)-benzofuranone (21)[21]:** 87% yield; bp 110 °C (bath temp, 1.0 Torr); IR (neat) 2934, 2870, 1774, 1729, 1174, 1122,

1082, 629 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.99 (d, J=6.7 Hz, 3H), 1.04 (d, J=6.8 Hz, 3H), 1.20—2.13 (m, 9H), 2.15—2.35 (m, 2H), 3.65 (ddd, J=3.8, 10.4, 11.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=18.97, 20.46, 23.85, 25.28, 26.60, 28.60, 30.06, 45.90, 52.17, 82.15, 177.60. Found: m/z 182.1206. Calcd for $C_{11}H_{18}O_2$: M 182.1305.

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