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The Hydroboration of 1-Alkylthio-1-alkynes, and Its Application to the Syntheses of *S*-Alkyl Alkanethioates and (*Z*)-1-Alkylthio-1-alkenes

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Hydroboration of 1-alkylthio-1-alkynes with dicyclohexylborane or bis(1,2-dimethylpropyl)borane proceeded smoothly, adding most of the dialkylboryl group to the α-position of the triple bond. The resulting alkenylboranes afforded either *S*-alkyl alkanethioates on a controlled oxidation with alkaline hydrogen peroxide in the presence of *N,N,N′,N′*-tetramethylethylenediamine or (*Z*)-1-alkylthio-1-alkenes on a basic protonolysis, successive treatments with methyllithium, copper(I) iodide and water in the presence of hexamethylphosphoric triamide.

Mono-hydroborations of 1-halo-1-alkynes[1] and 1-(trimethylsilyl)-1-alkynes[2] with dialkylboranes occur regio- and stereoselectively, giving corresponding (*Z*)-(1-substituted 1-alkenyl)dialkylboranes. These alkenylboranes are potentially useful synthetic intermediates.[3] Similarly, the hydroboration of 1-alkylthio-1-alkynes with dialkylboranes was expected to provide (*Z*)-(1-alkylthio-1-alkenyl)dialkylboranes. The sulfur-containing alkenylboranes seemed to be interesting intermediates for the synthesis of some organosulfur compounds.[4,5]

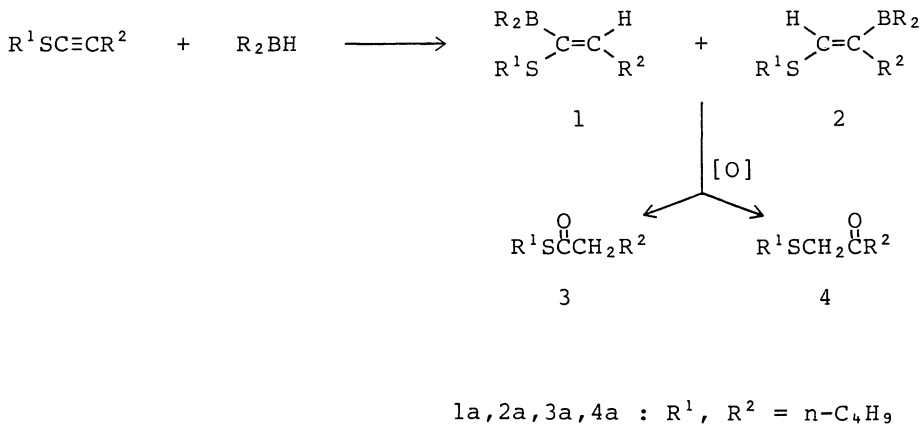
We wish to report a hydroboration of 1-alkylthio-1-alkynes with dialkylboranes and its applications to the syntheses of *S*-alkyl alkanethioates and (*Z*)-1-alkylthio-1-alkenes.

Results and Discussion

In preliminary experiments, 1-butylthio-1-hexyne (1 mmol) was hydroborated with dicyclohexylborane in tetrahydrofuran (THF) at 0 °C for 2 h. Completion of the reaction was confirmed by observing no evolution of hydrogen upon the addition of water to the reaction mixture and the disappearance of 1-butylthio-1-hexyne in the reaction mixture (examined by GLC).

The regioselectivity of the hydroboration was also examined by estimations of the amounts of *S*-butyl hexanethioate (**3a**) and 1-butylthio-2-hexanone (**4a**), subsequently formed by alkaline hydrogen peroxide oxidation of the hydroboration mixture (Scheme 1). Although the combined yield of **3a** and **4a** was greatly influenced by the oxidation conditions, a nearly quantitative yield was obtained by employing 3 mmol of hydrogen peroxide and 1 mmol of aqueous sodium hydroxide (**3a**; 80% and **4a**; 16% based on starting 1-butylthio-1-hexyne). Further, the combined yield became 100% by oxidation in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) under the same reaction conditions. The ratio **3a**/**4a**=83/17 (appearing in the above quantitative oxidation) suggested that the hydroboration of 1-butylthio-1-hexyne provided a mixture of alkenylboranes (**1a** and **2a**) in this ratio. **3a** and **4a** were isolated from the reaction mixture by column chromatography using a silica-gel column, and identified by the ^{1}H and ^{13}C NMR, IR, and mass spectra.

Bis(1,2-dimethylpropyl)borane also gave a satisfactory result, a 99% combined yield of **3a** and **4a** (72:28) upon a similar oxidation of the hydroboration mix-



1a,2a,3a,4a : R^1, R^2 = n-C_4H_9

Scheme 1.

Table 1. *S*-Alkyl Alkanethioates (**3**) and 1-Alkylthio-2-alkanones (**4**) Obtained by the Oxidation of the Hydroboration Products of 1-Alkylthio-1-alkynes

R of R_2BH	$R^1SC{\equiv}CR^2$			Ratio/%		Combined yield of products (**3** and **4**)	Isolated yield of **3**
	R^1	R^2		**3**	**4**	%[a]	%[b]
c-C_6H_{11}	*n*-C_4H_9	*n*-C_4H_9	**a**	83	17	100	77
	c-C_6H_{11}	*n*-C_4H_9	**b**	88	12	100	84
	C_6H_5	*n*-C_4H_9	**c**	95	5	90	82
	4-$CH_3C_6H_4$	*n*-C_4H_9	**d**	95	5	89	82
	4-ClC_6H_4	*n*-C_4H_9	**e**	97	3	72	68
	n-C_4H_9	*t*-C_4H_9	**f**	100	0	100	97
	n-C_4H_9	C_6H_5	**g**	86	14	100	83
C_5H_{11}[c]	*n*-C_4H_9	*n*-C_4H_9	**a**	72	28	99	
	c-C_6H_{11}	*n*-C_4H_9	**b**	81	19	99	
	C_6H_5	*n*-C_4H_9	**c**	90	10	85	
	4-$CH_3C_6H_4$	*n*-C_4H_9	**d**	88	12	90	
	4-ClC_6H_4	*n*-C_4H_9	**e**	91	9	72	
	n-C_4H_9	C_6H_5	**g**	86	14	100	

a) Determined by GLC and based on 1-alkylthio-1-alkyne employed. b) Isolated by column chromatography. c) C_5H_{11}: 1,2-Dimethylpropyl.

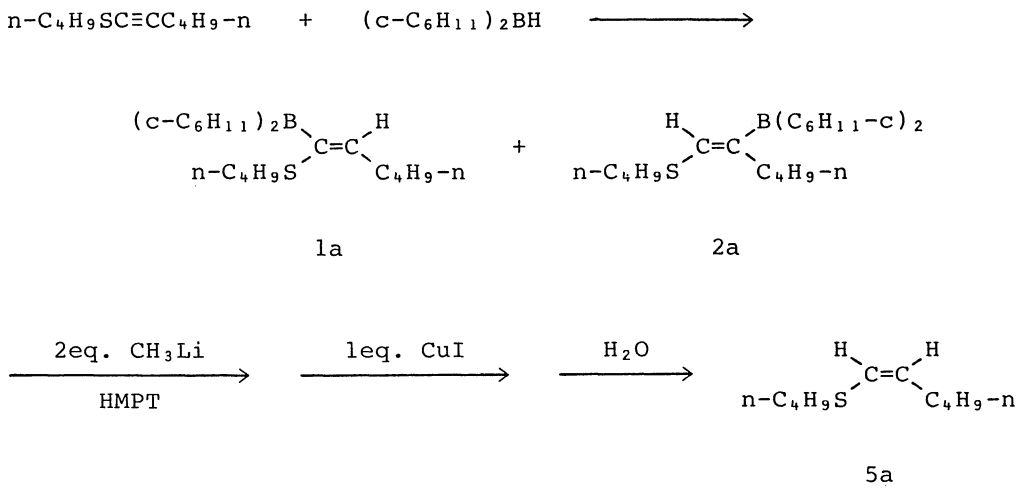
ture. However, other mono-hydroborating reagents, such as 9-borabicyclo[3.3.1]nonane (r.t., 24 h), 1,3,2-benzodioxaborole (70 °C, 4 h) and dibromoborane-dimethyl sulfide complex (0 °C, 3 h), gave unsatisfactory results: a 14—27% recovery of 1-butylthio-1-hexyne and a 6—47% combined yield of **3a** and **4a**.

To reveal the further scope of the hydroboration, reactions of several types of 1-alkylthio- or 1-arylthio-1-alkyne with dicyclohexylborane or bis(1,2-dimethylpropyl)borane were examined under similar conditions. As shown in Table 1, the hydroborations proceeded nearly quantitatively, except for the case of 1-(4-chlorophenylthio)-1-hexyne. The ratio of **3**/**4** varies from 72/28 to 100/0 depending on the structures of R^1 and R^2 of $R^1SC{\equiv}CR^2$. The electron-attracting character of R^1 and both the electron-releasing character and the bulkiness of R^2 seem to promote the orientation of the boron atom to the α-alkynyl carbon atom. This mono-hydroboration is inferior to those of the 1-halo-1-alkynes[1] and 1-(trimethylsilyl)-1-alkynes[2] regarding the regioselectivity of the addition of a dialkylboryl group to the α-alkynyl carbon atom. However, in all cases, highly pure **3** and **4** were isolated from the reaction mixtures by simple column chromatography. Thus, the present hydroboration-oxidation process provides a method for the synthesis of *S*-alkyl alkanethioates.

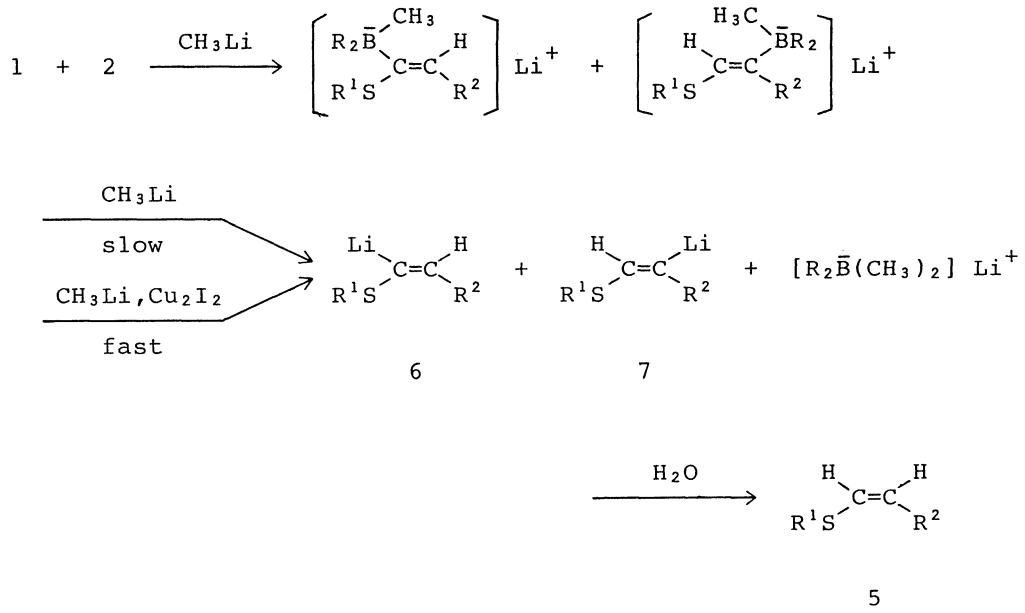
The stereochemistry of hydroboration was then examined by an analysis of the protonolysis product of the hydroboration mixture, obtained by a reaction of 1-butylthio-1-hexyne with dicyclohexylborane under conditions in which the boron atom on the alkenyl carbon atom of the alkenylboranes was protonolyzed with retention of configuration. Protonolysis with acetic acid, carried out at room temperature for 24 h, gave a 12% yield of (*Z*)-1-butylthio-1-hexene (**5a**) (examined by GLC). A treatment of the same reaction mixture with butyllithium in hexane and aqueous sodium hydroxide,[6] an effective method for converting (*E*)-(1-alkylthio-1-alkenyl)dialkylboranes into the corresponding (*E*)-1-alkylthio-1-alkenes,[5] increased the yield of **5a** only to 22%. By the way, Uchida et al. reported a transformation of the carbon-boron bond of (*Z*)-[1-(trimethylsilyl)-1-alkenyl]dicyclohexylboranes to the carbon-lithium bond with retention of configuration.[7] In a similar manner to Uchida's method, the reaction mixture was treated with two equimolar amounts of methyllithium in diethyl ether at 0 °C; it was then hydrolyzed with water. In this case, a 50% yield of **5a** was obtained. Further, the yield went up to 90% when the reaction mixture was treated with two equimolar amounts of methyllithium in diethyl ether in the presence of hexamethylphosphoric triamide (HMPT), used as a co-solvent, followed by the addition of a small amount of copper(I) iodide (0.1 mmol) at −30 °C. However, in this case **5a** was contaminated with many, but small, amounts of undefined by-products. Fortunately, the amounts of these contaminants became negligible when an equimolar amount of copper(I) iodide was employed under the same reaction conditions.

Similar treatments of the reaction mixtures, obtained by the reaction of some 1-alkylthio-1-alkynes with dialkylboranes, gave fairly good yields of 1-alkylthio-1-alkenes (**5**). They were isolated by column chromatography. These results are shown in Table 2.

Examinations of these 1-alkylthio-1-alkenes by GLC using a glass capillary column and by ^1H NMR spectra revealed that they had high isomeric purities. The *Z*-configuration was assigned to all 1-alkylthio-1-alkenes by coupling constants (J=9.2—11.2 Hz) of alkenyl protons in the ^1H NMR spectra. The signals



Scheme 2.



Scheme 3.

Table 2. (Z)-1-Alkylthio-1-alkenes (**5**) Obtained by Protonolysis of the Hydroboration Products of 1-Alkylthio-1-alkynes

R of R_2BH	$R^1SC{\equiv}CR^2$			Yield/%[a]
	R^1	R^2		**5**
c-C_6H_{11}	*n*-C_4H_9	*n*-C_4H_9	**a**	85
C_5H_{11}[b]	*n*-C_4H_9	*n*-C_4H_9	**a**	77
c-C_6H_{11}	*c*-C_6H_{11}	*n*-C_4H_9	**b**	86
	C_6H_5	*n*-C_4H_9	**c**	85
	4-$CH_3C_6H_4$	*n*-C_4H_9	**d**	78
	n-C_4H_9	*t*-C_4H_9	**f**	92
	n-C_4H_9	C_6H_5	**g**	84

a) Isolated by column chromatography and based on 1-alkylthio-1-alkyne employed. b) C_5H_{11}: 1,2-dimethylpropyl.

expected for the *E*-isomer were not detected in any case, indicating that the hydroboration of the triple bond proceeded stereoselectively during cis-addition. Thus, the present hydroboration-protonolysis process provides a new method for the synthesis of (*Z*)-1-alkylthio-1-alkenes.

Although the reaction mechanism of the above-mentioned protonolysis is not clear at present, it is speculated in the following way (Scheme 3). Thus, the addition of two equimolar amounts of methyllithium to the hydroborated mixture forms a mixture of alkenyllithiums (**6** and **7**) via ate-complexes. Both **6** and **7** are transformed into **5** during the subsequent hydrolysis. In the reaction carried out in a similar manner to the Uchida's method, the above transmetallation process is probably a not so fast reaction in the absence of copper(I) iodide. However, the formation of **6** and **7** is effectively accelerated by the addition of copper(I) iodide to give a fairly good yield of **5**.

In conclusion, the hydroboration of 1-alkylthio-1-alkynes with dicyclohexylborane or bis(1,2-dimethylpropyl)borane occurred completely during cis-addi-

tion, though the regioselectivity of the addition of the dialkylboryl group to the triple bond is not so excellent, and the resulting alkenylboranes can provide *S*-alkyl alkanethioates or (*Z*)-1-alkylthio-1-alkenes. 1-Alkylthio-1-alkenes are useful intermediates for organic synthesis,[8] and attempts regarding their stereoselective synthesis have been reported.[9] The authors previously reported a highly stereospecific synthesis of (*E*)-1-alkylthio-1-alkenes via (*E*)-(1-alkylthio-1-alkenyl)boranes.[5] Thus, we are in the position to stereoselectively synthesize (*Z*)- or (*E*)-1-alkylthio-1-alkenes via the corresponding (1-alkylthio-1-alkenyl)boranes by employing either the present or the previous method.

Experimental

Instruments. The ^{1}H and ^{13}C NMR spectra were recorded on a Jeol FX-200 (200 MHz) spectrometer and obtained from a $CDCl_3$ solution containing TMS as the internal standard. The IR spectra (film) were recorded on a Hitachi 285 spectrometer. Mass spectra were recorded on a Hitachi M-52 mass spectrometer. GLC analyses using a glass capillary column were carried out with a Shimadzu GC-mini 2-gas chromatograph equipped with a flame ionization detector and a precision needle valve (column: PEG-HT, 50m×0.2 mm).

Materials. Alkenes, alkynes, solvents, and some of the reagents employed in the reactions were used after purifying by methods generally employed in similar organoborane chemistry. The alkanesulfenyl chlorides used in the preparation of starting 1-alkylthio-1-alkynes were prepared by a method described in the literature.[10] Commercial butyllithium (1.6 mol dm^{-3} solution) in hexane and methyllithium (1.4 mol dm^{-3} solution) in diethyl ether were used without any purification. A THF solution of BH_3 was prepared by a method described in the literature.[11] TMEDA and HMPT were distilled under vacuum from calcium hydride, and stored over Molecular Sieves-4A. Commercial copper(I) iodide was used after drying in a vacuum desicator containing phosphorus pentaoxide. 1-Alkylthio-1-alkynes were prepared in the following way: In an argon-flushed dry 100-ml round-bottomed flask, 1-alkyne (40 mmol) and 40 ml of dry THF were charged. To the stirred solution was slowly added 25 ml of butyllithium (1.6 mol dm^{-3} solution) in hexane (40 mmol) at −70 °C, and the reaction mixture was stirred for 0.5 h at this temperature. Alkanesulfenyl chloride (40 mmol) was then added to the resulting 1-alkynyllithium at −70 °C. After stirring for 0.5 h at −70 °C, the reaction mixture was allowed to warm to room temperature and stirred overnight. After the work-up, 1-alkylthio-1-alkyne was isolated by vacuum distillation. Their ^{1}H and ^{13}C NMR, IR, and mass spectral data were coincident with those of expected structures.

Representative Procedure. Synthesis of *S*-Butyl Hexanethioate (3a). In an argon-flushed dry 25-ml round-bottomed flask equipped with a sample inlet with a serum cap and a magnetic stirring bar, 0.17 g of 1-butylthio-1-hexyne (1 mmol) was added to dicyclohexylborane (1 mmol) in THF at 0 °C. The reaction mixture was stirred for 2 h at 0 °C, and oxidized by successive additions of 0.5 ml of TMEDA, 0.33 ml of 3 mol dm^{-3} aqueous sodium hydroxide (1 mmol) and 0.31 ml of 30% hydrogen peroxide (3 mmol) at 0 °C for 1 h. The resulting products were extracted with diethyl ether, and the extract was washed with brine. The organic layer was analyzed by GLC (5% FFAP on Diasolid M) using the internal-standard method.

In the preparative reaction, the amounts of the reagents and solvents used were ten-times those used in the analytical reaction. The worked-up solution was dried over anhydrous sodium sulfate, and concentrated on a rotary evaporator under reduced pressure. The residue was put on a silica-gel column. First, 1.45 g of *S*-butyl hexanethioate (77% yield) was isolated; then, 0.28 g of 1-butylthio-2-hexanone (15%) was isolated by elution with benzene.

Synthesis of (*Z*)-1-Butylthio-1-hexene (5a). After the hydroboration of 1-butylthio-1-hexyne (1 mmol) with dicyclohexylborane (1 mmol) was carried out (as described above), 0.5 ml of dry HMPT was added to the reaction mixture at 0 °C, followed by the addition of 1.43 ml of a 1.4 mol dm^{-3} solution of methyllithium (2 mmol) in diethyl ether. After stirring for 0.5 h at 0 °C, the solution was cooled to −30 °C, and 0.19 g of copper(I) iodide (1 mmol) was then added to the solution through a sample inlet under a stream of argon. The resulting dark-brown solution was stirred for 0.5 h at −30 °C and for 0.5 h at 0 °C; then, 1 ml of water was added at this temperature. After stirring for 1 h at 0 °C, the reaction mixture was analyzed by GLC (5% FFAP on Diasolid M) using the internal-standard method.

The scale of the preparative reaction was the same as that described regarding the oxidation reaction. After filtration of the reaction mixture for removing copper compounds, the filtrate was extracted with diethyl ether. The extract was washed with cold brine, and dried over anhydrous potassium carbonate in a refrigerator. The solvent was removed on a rotary evaporator under reduced pressure, and the residue was put on a basic aluminium oxide column, fitted with a jacket cooled by circulation of chilled ethanol (−15—−20 °C). 1.27 g of (*Z*)-1-butylthio-1-hexene was isolated by elution with pentane (85% yield).

The products were identified by following data.

***S*-Butyl Hexanethioate (3a):**[12] ^{1}H NMR ($CDCl_3$) δ= 0.80—0.98 (m, 6H), 1.20—1.76 (m, 10H), 2.53 (t, J=7.3 Hz, 2H), and 2.87 (t, J=7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=13.60, 13.86, 21.95, 22.33, 25.40, 28.49, 31.12, 31.68, 44.12, and 199.81 (>C=O); IR (film) 1690 (C=O) cm^{-1}; MS m/z 188 (M^+).

1-Butylthio-2-hexanone (4a): ^{1}H NMR δ=0.84—1.00 (m, 6H), 1.14—1.75 (m, 8H), 2.48 (t, J=7.3 Hz, 2H), 2.61 (t, J=7.3 Hz, 2H), and 3.19 (s, 2H); ^{13}C NMR δ=13.60, 13.84, 21.87, 22.27, 26.07, 31.03, 31.85, 39.91, 41.05, and 206.23 (>C=O); IR 1730 and 1710 (C=O) cm^{-1}; MS m/z 188 (M^+); Found: C, 63.57; H, 10.56%. Calcd for $C_{10}H_{20}OS$: C, 63.77; H, 10.70%.

***S*-Cyclohexyl hexanethioate (3b):**[12] ^{1}H NMR δ=0.82—0.98 (m, 3H), 1.00—2.00 (m, 16H), 2.50 (t, J=7.3 Hz, 2H), and 3.37—3.60 (m, 1H); ^{13}C NMR δ=13.89, 22.33, 25.40, 25.57, 25.95 (-CH_2-, 2C), 31.12, 33.08 (-CH_2-, 2C), 42.07 (>CH-), 44.20, and 199.57 (>C=O); IR 1690 (C=O) cm^{-1}; MS m/z 214 (M^+).

1-Cyclohexylthio-2-hexanone (4b): ^{1}H NMR δ=0.84—0.99 (m, 3H), 1.15—2.05 (m, 15H), 2.61 (t, J=7.3 Hz, 2H), and 3.23 (s, 2H); ^{13}C NMR δ=13.86, 22.30, 25.72, 25.92 (-CH_2-, 2C), 26.10, 33.19 (-CH_2-, 2C), 39,65, 40.00, 43.68 (>CH-), and 206.84 (>C=O); IR 1715 (C=O) cm^{-1}; MS m/z 214 (M^+); Found: C, 67.11; H, 10.28%. Calcd for $C_{12}H_{22}OS$:

C, 67.23; H, 10.34%.

S-Phenyl Hexanethioate (3c):[12] ^{1}H NMR δ=0.82—0.97 (m, 3H), 1.24—1.45 (m, 4H), 1.60—1.80 (m, 2H), 2.65 (t, J=7.3 Hz, 2H), and 7.40 (s, 5H); ^{13}C NMR δ=13.89, 22.33, 25.28, 31.09, 43.68, 127.95 (>C=), 129.12 (-CH=, 2C), 129.26 (-CH=), 134.46 (-CH=, 2C), and 197.53 (>C=O); IR 1715 (C=O), 745, and 690 cm^{-1}; MS m/z 208 (M^+).

1-Phenylthio-2-hexanone (4c): ^{1}H NMR δ=0.80—1.00 (m, 3H), 1.13—1.70 (m, 4H), 2.58 (t, J=7.3 Hz, 2H), 3.66 (s, 2H), and 7.11—7.41 (m, 5H); IR 1715 (C=O), 735, and 690 cm^{-1}; MS m/z 208 (M^+); Found: C, 69.01; H, 7.68%. Calcd for $C_{12}H_{16}OS$: C, 69.18; H, 7.74%.

S-(4-Methylphenyl) Hexanethioate (3d): ^{1}H NMR δ= 0.83—0.97 (m, 3H), 1.20—1.45 (m, 4H), 1.60—1.80 (m, 2H), 2.36 (s, 3H), 2.63 (t, J=7.3 Hz, 2H), and 7.06—7.33 (m, 4H); ^{13}C NMR δ=13.89, 21.31, 22.33, 25.31, 31.12, 43.59, 124.41 (>C=), 129.96 (-CH=, 2C), 134.43 (-CH=, 2C), 139.51 (>C=), and 198.06 (>C=O); IR 1715 (C=O) and 810 cm^{-1}; MS m/z 222 (M^+); Found: C, 70.02; H, 8.08%. Calcd for $C_{13}H_{18}OS$: C, 70.22; H, 8.16%.

1-(4-Methylphenylthio)-2-hexanone (4d): ^{1}H NMR δ= 0.87 (t, J=7.3 Hz, 3H), 1.10—1.70 (m, 4H), 2.30 (s, 3H), 2.56 (t, J=7.3 Hz, 2H), 3.60 (s, 2H), and 6.90—7.45 (m, 4H); ^{13}C NMR δ=13.81, 21.02, 22.22, 25.87, 40.35, 44.53, 129.88 (-CH=, 2C), 130.43 (-CH=, 2C), 131.02 (>C=), 137.12 (>C=), and 205.86 (>C=O); IR 1715 (C=O) and 805 cm^{-1}; MS m/z 222 (M^+); Found: C, 70.07; H, 8.09%. Calcd for $C_{13}H_{18}OS$: C, 70.22; H, 8.16%.

S-(4-Chlorophenyl) Hexanethioate (3e): ^{1}H NMR δ= 0.85—0.97 (m, 3H), 1.20—1.46 (m, 4H), 1.58—1.80 (m, 2H), 2.64 (t, J=7.3 Hz, 2H), and 7.24—7.47 (m, 4H); ^{13}C NMR δ=13.84, 22.30, 25.22, 31.09, 43.74, 126.46 (>C=), 129.38 (-CH=, 2C), 135.66 (-CH=, 2C, and >C=), and 196.92 (>C=O); IR 1715 (C=O), 820, and 745 cm^{-1}; MS m/z 242 and 244 (M^+); Found: C, 59.19; H, 6.17%. Calcd for $C_{12}H_{15}ClOS$: C, 59.37; H, 6.23%.

S-Butyl 3,3-Dimethylbutanethioate (3f): ^{1}H NMR δ= 0.84—1.00 (m, 3H), 1.03 (s, 9H), 1.25—1.65 (m, 4H), 2.42 (s, 2H), and 2.85 (t, J=7.3 Hz, 2H); ^{13}C NMR δ=13.60, 21.98, 28.81, 29.72 (CH_3-, 3C), 31.56 (-C-), 31.68, 56.85, and 198.14 (>C=O); IR 1690 (C=O) cm^{-1}; MS m/z 188 (M^+); Found: C, 63.52; H, 10.56%. Calcd for $C_{10}H_{20}OS$: C, 63.77; H, 10.70%.

S-Butyl 2-Phenylethanethioate (3g):[13] ^{1}H NMR δ= 0.83—0.98 (m, 3H), 1.20—1.60 (m, 4H), 2.85 (t, J=7.3 Hz, 2H), 3.80 (s, 2H), and 7.12—7.47 (m, 5H); ^{13}C NMR δ=13.57, 21.95, 28.96, 31.44, 50.54, 127.31 (-CH=), 128.59 (-CH=, 2C), 129.52 (-CH=, 2C), 133.79 (>C=), and 197.53 (>C=O); IR 1695 (C=O) and 710 cm^{-1}; MS m/z 208 (M^+).

1-Phenyl-2-butylthioethanone (4g): ^{1}H NMR δ=0.85—0.98 (m, 3H), 1.20—1.70 (m, 4H), 2.56 (t, J=7.3 Hz, 2H), 3.78 (s, 2H), 7.35—7.63 (m, 3H), and 7.90—8.02 (m, 2H); ^{13}C NMR δ=13.63, 21.87, 31.00, 32.03, 37.08, 128.62 (-CH=, 2C), 128.74 (-CH=, 2C), 133.26 (-CH=), 135.22 (>C=), and 194.52 (>C=O); IR 1680 (C=O), 730, and, 690 cm^{-1}; MS m/z 208 (M^+); Found: C, 68.95; H, 7.64%. Calcd for $C_{12}H_{16}OS$: C, 69.18; H, 7.74%.

(Z)-1-Butylthio-1-hexene (5a): ^{1}H NMR δ=0.82—1.00 (m, 6H), 1.15—1.80 (m, 8H), 2.02—2.20 (m, 2H), 2.65 (t, J=6.8 Hz, 2H), 5.54 (dt, J=9.2 and 7.3 Hz, 1H), and 5.89 (d, J=9.2 Hz, 1H); ^{13}C NMR δ=13.67, 13.96, 21.72, 22.33, 28.87, 31.18, 32.42, 33.59, 124.95 (-CH=), and 129.53 (-CH=); IR 740 cm^{-1}; MS m/z 174 (M^+); Found: C, 69.56; H, 11.61%. Calcd for $C_{10}H_{20}S$: C, 69.69; H, 11.70%.

(Z)-1-Cyclohexylthio-1-hexene (5b): ^{1}H NMR δ=0.80—1.00 (m, 3H), 1.10 —2.30 (m, 16H), 2.60—2.92 (m, 1H), 5.55 (dt, J=9.7 and 7.3 Hz, 1H), and 5.97 (d, J=9.7 Hz, 1H); ^{13}C NMR δ=13.96, 22.33, 25.71, 26.05 (-CH_2-, 2C), 28.87, 31.18, 33.78 (-CH_2-, 2C), 45.63 (>CH-), 123.03 (-CH=), and 129.89 (-CH=); IR 740 cm^{-1}; MS m/z 198 (M^+); Found: C, 72.49; H, 11.07%. Calcd for $C_{12}H_{22}S$: C, 72.65; H, 11.18%.

(Z)-1-Phenylthio-1-hexene (5c): ^{1}H NMR δ=0.85—1.00 (m, 3H), 1.12—1.60 (m, 4H), 2.08—2.44 (m, 2H), 5.82 (dt, J=9.2 and 7.3 Hz, 1H), 6.18 (d, J=9.2 Hz, 1H), and 7.10—7.50 (m, 5H); ^{13}C NMR δ=13.93, 22.30, 28.82, 31.18, 122.50 (-CH=), 126.05 (-CH=), 128.70 (-CH=, 2C), 128.92 (-CH=, 2C), 133.68 (-CH=), and 136.53 (>C=); IR 760, 735, and 690 cm^{-1}; MS m/z 192 (M^+); Found: C, 74.80; H,8.28%. Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39%.

(Z)-1-(4-Methylphenylthio)-1-hexene (5d): ^{1}H NMR δ= 0.85—1.00 (m, 3H), 1.10—1.60 (m, 4H), 2.10—2.40 (m, 2H), 2.31 (s, 3H), 5.75 (dt, J=9.2 and 7.3 Hz, 1H), 6.14 (d, J=9.2 Hz, 1H), and 6.96—7.37 (m, 4H); IR 805 and 755 cm^{-1}; MS m/z 206 (M^+); Found: C, 75.51; H, 8.67%. Calcd for $C_{13}H_{18}S$: C, 75.66; H, 8.79%.

(Z)-1-Butylthio-3,3-dimethyl-1-butene (5f): ^{1}H NMR δ= 0.91 (t, J=7.3 Hz, 3H), 1.15 (s, 9H), 1.25—1.75 (m, 4H), 2.62 (t, J=7.3 Hz, 2H), 5.44 (d, J=11.2 Hz, 1H), and 5.74 (d, J=11.2 Hz, 1H); ^{13}C NMR δ=13.67, 21.72, 29.67 (CH_3-, 3C), 32.20, 33.42 (-C-), 35.05, 123.25 (-CH=), and 137.75 (-CH=); IR 740 cm^{-1}; MS m/z 174 (M^+); Found: C, 69.54; H, 11.59%. Calcd for $C_{10}H_{20}S$: C, 69.69; H, 11.70%.

(Z)-1-Butylthio-2-phenylethene (5g): ^{1}H NMR δ=0.92 (t, J=7.3 Hz, 3H), 1.30—1.80 (m, 4H), 2.78 (t, J=7.3 Hz, 2H), 6.24 (d, J=11.2 Hz, 1H), 6.42 (d, J=11.2 Hz, 1H), and 7.10—7.60 (m, 5H); ^{13}C NMR δ=13.64, 21.69, 32.30, 35.58, 125.20 (-CH=), 126.53 (-CH=), 127.70 (-CH=), 128.19 (-CH=, 2C), 128.58 (-CH=, 2C), and 137.04 (>C=); IR 770, 730, and 690 cm^{-1}; MS m/z 192 (M^+); Found: C, 74.78; H, 8.28%. Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39%.

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