3 H), 0.04 (s, 3 H), 0.41 (d, 3 H, J = 7.0 Hz), 0.81 (s, 9 H), 1.33 (d, 3 H, J = 7.2 Hz), 2.77 (s, 3 H), 2.74-2.94 (m, 1H), 3.44 (dd, 1 H, J = 10.0 Hz, 6.0 Hz), 3.65 (dd, 1 H, J = 16.0 Hz, 10.0 Hz), 4.1-4.44 (dq, 1 H, J = 7.2 Hz, 4.8 Hz), 4.84 (d, 1 H, J = 4.8 Hz), 7.2-7.4 (m, 5 H); IR ($CHCl_3$) 2.68, 2.75-3.2, 3.33-3.6, 6.2, 6.85, 8.0, 9.2, 12.0, 14.3 μm; UV 95% ethanol) λ_{max} 259 nm (ε 85), 264 nm (ε 85); chemical ionization mass spectrum, m/e 365 (M^+), 350, 308, 258, 216, 148; **9a** exhibited a positive CD curve, λ_{max} 222 nm (c 1.53 × 10^{-4} M, 95% ethanol).

Anal. Calcd for $C_{20}H_{35}NO_3Si$: C, 65.71; H, 9.65; N, 3.83. Found: C, 65.85; H, 9.62; N, 3.81.

Preparation of (1′*S*,2′*R*,2*S*)-*N*,2-Dimethyl-*N*-(2′-hydroxy-1′-methyl-2′-phenylethyl)-3-hydroxypropionamide (9b) (from 9a). Prepared from **9a** (36.5 mg, 0.1 mmol) by using method B described for the preparation of **8b**. **9b** (colorless oil) was obtained as a 90:10 mixture of two conformational isomers after flash chromatography (silica gel, 5% methanol in ethyl acetate) and distillation (bp 90-95 °C (0.2 mm)); ^1H NMR ($CDCl_3$, 200 MHz) (major isomer) δ 1.06 (d, 3 H, J = 7.0 Hz), 1.25 (d, 3 H, J = 7.2 Hz), 1.72 (br s, 1 H), 2.72 (tq, 1 H, J = 7.0, 4.8 Hz), 2.8 (s, 3 H), 3.43-3.74 (m, 3 H), 4.6 (dq, 1 H, J = 7.2 Hz, 4.2 Hz), 4.84 (d, 1 H, J = 4.2 Hz), 7.24-7.5 (m, 5 H); (minor isomer) δ 0.67 (d, 3 H, J = 7.0 Hz), 1.39 (d, 3 H, J = 7.2 Hz), 1.72 (br s, 1 H), 2.72 (tq, 1 H, J = 7.0 Hz, 4.8 Hz), 2.88 (s, 3 H), 3.43-3.74 (m, 3 H), 4.6 (dq, 1 H, J = 7.2 Hz, 4.2 Hz), 4.84 (d, 1 H, J = 4.2 Hz), 7.24-7.5 (m, 5 H); IR ($CHCl_3$) 2.78 , 2.85-3.2, 3.3-3.55, 6.2, 7.0, 9.6, 14.3 μm; UV (95% ethanol) λ_{max} 258 nm (ε 209), 264 nm (ε 180); chemical ionization mass spectrum, m/e 251 (M^+), 234, 148; **9b** exhibited a positive CD curve, λ_{max} 222 nm (2.39 × 10^{-4} M, ethanol).

Anal. Calcd for $C_{14}H_{21}NO_3$: C, 66.91; H, 8.42; N, 5.57. Found: C, 67.22; H, 8.59; N, 5.43.

Preparation of (1′*R*,2′*S*,2*S*)-*N*-Methyl-*N*-(2′-hydroxy-1′-methyl-2′-phenylethyl)-2-phenylbutyramide (12). A stirred solution containing 2-phenylbutyroyl chloride (0.365 g, 2 mmol) in dry toluene (5 mL) was cooled to 0 °C and a solution containing triethylamine (0.202 g, 2 mmol) in dry toluene (5 mL) was added. The resulting mixture was allowed to warm to room temperature and stirred for 3 h. The solvents were then removed and the ethylphenylketene (**11**) was distilled and stored at -78 °C (bp 75-77 °C at 2 mm). To **11** in dry toluene (10 mL) at -78 °C was added a solution of *d*-ephedrine (0.413 g, 2.5 mmol) in dry toluene (5 mL). The resulting mixture was stirred at -78 °C for 15 min and allowed to warm to room temperature. The solution was washed with 2 N HCl (1 × 25 mL), saturated sodium bicarbonate (1 × 25 mL), and water (1 × 25 mL). It was then dried and evaporated under reduced pressure to give a 75:25 mixture of two diastereoisomers. The major isomer was obtained by fractional crystallization from 30% ethyl acetate in hexane (mp 118-119 °C, 375 mg, 60%): ^1H NMR ($CDCl_3$, 200 MHz) δ 0.81 (t, 3 H, J = 7.2 Hz), 1.16 (d, 3 H, J = 7.2 Hz), 1.56-1.8 (m, 1 H), 1.94-2.18 (m, 1 H), 2.66 (s, 3 H), 3.51 (dd, 1 H, J = 8.0 Hz, 6.0 Hz), 3.99 (d, 1 H, J = 2.8 Hz), 4.48 (dq, 1 H, J = 7.2 Hz, 3.2 Hz), 4.82 (dd, 1 H, J = 3.2 Hz, 2.8 Hz), 7.33-7.4 (m, 10 H); IR ($CHCl_3$) 2.78, 2.82-3.2, 3.25-3.55, 6.2, 6.9, 7.15, 8.3, 14.4 μm; UV (95% ethanol) λ_{max} 252 nm (ε 510), 259 nm (ε 570), 264 nm (ε 405); chemical ionization mass spectrum, m/e 311 (M^+), 294, 204, 177, 148.

Anal. Calcd for $C_{20}H_{25}NO_2$: C, 77.14; H, 8.09; N, 4.50. Found: C, 77.19; H, 8.10; N, 4.53.

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Organotin-Mediated Selective Desulfurization: Tri-*n*-butyltin Hydride Reduction of Unsymmetric Sulfides

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Tri-*n*-butyltin hydride (TBTH) has been evaluated as a selective agent for the reductive cleavage of one C-S bond in unsymmetric sulfides **1** ($R \neq R^1$). Sulfides **1** [where combinations of R and R^1 included primary, secondary, tertiary, benzylic, phenyl, allylic, and α-(to carbonyl) carbon bound to sulfur] were each reacted with 1 equiv of TBTH in the presence of AIBN initiator. Reduction by TBTH occurs initially at the R^1-S bond (where R^1 can form the more stable carbon radical intermediate) in sulfide **1** selectively, if not specifically, to yield hydrocarbon **4** and tributylstannyl alkyl sulfide **3**. However, this specificity can be negated by an enhanced reactivity toward reduction by TBTH which the C-S bond in **3** exhibits, producing hydrocarbon **6** and bis(tributyltin) sulfide. The degree of selectivity in desulfurization is determined by the competition between unsymmetric sulfide **1** and alkyl organotin sulfide **3** for TBTH. The reduction of secondary and primary alkyl C-S bonds in **1** is so slow as to discount the synthetic utility of trialkyltin hydride reduction for such sulfides.

The broad distribution of sulfur in natural products and medicinal compounds has prompted considerable effort in the synthetic aspects of organosulfur chemistry. Work in this laboratory has been directed toward the development of methodology for the manipulation of specific C-S bonds in molecules wherein several are present. One area of special interest to us has been the reduction of unsymmetric sulfides **1**.[1]

We have reported the use of tri-*n*-butyltin hydride (hereafter abbreviated TBTH) as an effective and selective reducing agent for 1,3-dithiolanes.[2] The observation that 1 equiv of this organotin reagent could cleave as well as discriminate between primary, secondary, and benzylic C-S bonds implied it could be a general, yet selective, desulfurization agent. We now report the scope and limitations of the use of TBTH for selective reduction of unsymmetric sulfides **1**.[3]

As in many reactions of TBTH, the reductions we now describe appear to be free radical processes, initiated by

(1) Lithium metal in ethylamine solution has been reported to reduce certain unsymmetric sulfides selectively: (a) Truce, W. E.; Tate, D. P.; Burdge, D. N. *J. Am. Chem. Soc.* **1960**, *82*, 2872. (b) Stotter, P. L.; Hornish, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 4444. Lithium hydride has likewise been used: Blackburn, G. M.; Ollis, W. D.; Smith, C.; Sutherland, J. *J. Chem. Soc., Chem. Commun.* **1969**, 99.

(2) Gutierrez, C. G.; Stringham, R. A.; Nitasaka, T.; Glasscock, K. G. *J. Org. Chem.* **1980**, *45*, 3393.

(3) For examples of attempted reduction of sulfides by several equivalents of triorganotin hydride, see: (a) Pang, M.; Becker, E. I. *J. Org. Chem.* **1964**, *29*, 1948. (b) McIntosh, J. M.; Schram, C. K. *Can. J. Chem.* **1977**, *55*, 3755. (c) Haskell, T. H.; Woo, P. W. K.; Watson, D. R. *J. Org. Chem.* **1977**, *42*, 1302.

0022-3263/84/1949-5206$01.50/0

Table I. Reaction of Unsymmetic Dialkyl Sulfides with 1 equiv of Tri-*n*-butyltin Hydride[a]

	RSR[1]		% unreacted sulfide 1[b]	products,[b] % yield			
	R	R^1		R^1H, 4	RH, 6	Bu_3SnSR, 3	$(Bu_3Sn)_2S$
1a	CH_3	n-C_6H_{13}	100	0	0	0	0
1b	CH_3	c-C_6H_{11}	89[c]	10	*d*	5[b]	5
1c	CH_3	i-C_3H_7	75	*d*	*d*	10[b]	13
1d	CH_3	t-C_4H_9	33	*d*	*d*	30	34
1e	C_2H_5	t-C_4H_9	41[c]	*d*	*d*	18	41
1f	i-C_3H_7	t-C_4H_9	50	*d*	*d*	0	51

[a] Reactions were run 45 h in refluxing benzene, with 2,2′-azobis(isobutyronitrile) used as initiator. [b] By NMR. [c] By GLC analysis. [d] Gaseous products not analyzed.

Table II. Reduction of Benzyl Sulfides 7 by 1 equiv of Tri-*n*-butyltin Hydride[a]

	$PhCH_2SR$, R	reactn time, h	% unreacted 7[b]	products,[b] % yield		
				toluene	RH, 6	Bu_3SnSR, 3
7a	CH_3	0.4	0	100	0	100 (79)
7b	C_2H_5	0.4	15	85	*c*	70
7c	n-C_6H_{13}	0.5	16	84, 80[d]	16, 15[d]	68 (57)
7d	c-C_6H_{11}	1.8	30	70	30	44 (25)
7e	i-C_3H_7	1.2	44	56	*c*	12
7f	t-C_4H_9	3.1	50	50	*c*	0

[a] Reactions were conducted in refluxing benzene, using 2,2′-azobis(isobutyronitrile) as initiator. [b] The yields were determined by NMR. The values in parentheses are isolated yields. [c] Gaseous product was not analyzed. [d] By GLC analysis.

2,2′-azobis(isobutyronitrile) (AIBN) and inhibited by hydroquinone.[4] The reactions seem to proceed by homolytic substitution at sulfur in unsymmetric sulfide 1 by the tributylstannyl radical 2 (the formation of which is initiated by AIBN). Since 1 has two different C–S bonds, reaction with organotin radical 2 can conceivably occur via the two pathways outlined (propagation steps only) by eq 1 and 2.

$$\underset{1}{RSR^1} + \underset{2}{Bu_3Sn\cdot} \rightarrow \underset{3}{RSSnBu_3} + R^1\cdot \xrightarrow{\text{TBTH}} \underset{4}{R^1H} + 2 \quad (1)$$

$$\underset{1}{RSR^1} + \underset{2}{Bu_3Sn\cdot} \quad \underset{5}{Bu_3SnSR^1} + R\cdot \xrightarrow{\text{TBTH}} \underset{6}{RH} + 2 \quad (2)$$

The intent of the present study was to establish the degree of selectivity between the pathways summarized by eq 1 and 2 which TBTH might exhibit in the reductive cleavage of unsymmetric sulfides 1.

Results and Discussion

We have reacted a variety of unsymmetric sulfides with 1 equiv of TBTH in refluxing benzene, using 2,2′-azobis(isobutyronitrile) as initiator.

Dialkyl Sulfides. A set of unsymmetric dialkyl sulfides (where R and R^1 included primary, secondary, and tertiary carbon bound to sulfur) was reduced. Table I summarizes these results. The extent of reaction was disappointingly low with sulfides **1a–c**, where R was methyl and R^1 either primary or secondary alkyl. The hydride effected essentially no reduction in the first 10 h and little (0–25%) after 45 h. The final reaction mixtures consisted of unreacted 1 and TBTH, small amounts of hydrocarbons 4 (except where gaseous), methyl tributyltin sulfide, and/or bis(tributyltin) sulfide. Longer reaction times did not result in synthetically useful amounts of products. For example, cyclohexyl methyl sulfide (**1b**) underwent only 20% reduction after 73 h. We observed similarly limited reactions when triphenyltin hydride rather than TBTH was employed as the reducing agent.

The *tert*-butyl sulfides **1d–f** reacted more extensively with TBTH; some 50–67% of starting sulfide having been consumed after 45 h.

Benzyl Sulfides. We expected that reduction of unsymmetric benzyl sulfides 7 would proceed predominantly via the process (eq 3) involving the intermediacy of a resonance-stabilized benzylic radical. The alternative, eq 4, would require the generation of an alkyl radical intermediate. The results are summarized in Table II. These reductions were extensive and rapid, consuming the full equivalent of reducing agent in under 2 h (in several cases, under 30 min). The major hydrocarbon product in each case was toluene.

$$\underset{7}{RSCH_2Ph} + \underset{\text{(TBTH)}}{Bu_3SnH} \rightarrow PhCH_3 + 3 \quad (3)$$

$$\underset{7}{RSCH_2Ph} + \underset{\text{(TBTH)}}{Bu_3SnH} \rightarrow 6 + \underset{\mathbf{3a}}{Bu_3SnSCH_2Ph} \quad (4)$$

The reduction of methyl benzyl sulfide (**7a**) was specific, giving a quantitative yield of toluene and methyl tributyltin sulfide. The reductions of sulfides **7b–f** were, however, more complex. The reaction mixtures consisted of the products expected from eq 3 and 4 except (a) no benzyl tributyltin sulfide (**3a**) was observed, (b) the presence of varying amounts of bis(tributyltin) sulfide was detected, and (c) increasing quantities of unreacted benzyl sulfides 7 were recovered.[5]

Since we had previously observed such limited reduction of the dialkyl sulfides (Table I), it seemed unlikely that hydrocarbons 6 were produced by a direct reduction of the S–R bond in benzyl sulfides 7 as represented by eq 4. That no benzyl tributyltin sulfide (**3a**) was detected in these experiments also made eq 4 suspect.

A more probable explanation is the initial specific reduction of the benzylic C–S bond by the organotin hydride as shown in eq 3, followed by a competition between any

(4) Kuivila, H. G. *Synthesis* **1970**, 499.

(5) Addition of a second equivalent of tri-*n*-butyltin hydride resulted in complete reduction of 7 to toluene, hydrocarbon 6, and bis(tributyltin) sulfide.

Table III. Reduction of Alkyl Tri-*n*-butyltin Sulfides 3 by 1 equiv of Tri-*n*-butyltin Hydride[a]

	Bu_3SnSR, R	reactn time, h	products,[b] % yield RH, 6	$(Bu_3Sn)_2S$
3a	$PhCH_2$	0.10	95	100 (89)
3b	t-C_4H_9	0.17	[c]	100 (96)
3c	i-C_3H_7	1.67	[c]	100 (90)
3d	c-C_6H_{11}	2.17	90	100 (92)
3e	n-C_6H_{13}	35	92	100 (97)
3f	C_2H_5	35	[c]	100 (96)
3g	CH_3	40	[c]	100 (98)
3h	Ph[d]	43	0	0

[a] Reaction conducted in refluxing benzene, using 2,2′-azobis(isobutyronitrile) as initiator. [b] NMR yield (isolated yield). [c] Gaseous product not analyzed. [d] Benzene-d_6 used as reaction solvent.

unreacted benzyl sulfide 7 and the alkyl tributyltin sulfide 3 for remaining tributyltin hydride, eq 5. This would also

$$\underset{\mathbf{3}}{Bu_3SnSR} + Bu_3SnH \rightarrow \underset{\mathbf{6}}{RH} + (Bu_3Sn)_2S \qquad (5)$$

account for the generation of bis(tributyltin) sulfide. If the process represented by eq 5 were as fast as, or faster than, eq 3, TBTH would be consumed at a faster rate than sulfide substrate 7, explaining the incomplete reduction of benzyl sulfides **7b–f**.

Tributyltin Sulfides. To test this premise, several alkyl tributyltin sulfides 3 were prepared[6] (eq 6) and

$$\underset{\mathbf{9}}{2RSH} + (Bu_3Sn)_2O \rightarrow \underset{\mathbf{3}}{2RSSnBu_3} + H_2O \qquad (6)$$

subsequently reduced with 1 equiv of TBTH. The results are shown in Table III. In sharp contrast to the dialkyl sulfides (Table I), the tributyltin alkyl sulfides 3 reduced, surprisingly rapidly, via eq 5.[7] Only phenyl tributyltin sulfide (**3h**) failed to react. Also apparent from Table III is that the ease of reduction of sulfides 3 parallels the stabilities of the carbon radical intermediates believed to be formed: benzylic > tertiary > secondary > primary. This is consonant with the amounts of hydrocarbon product RH (6) reported in the reduction of benzylic sulfides, Table II.[8]

The combination of eq 6 and 5 represents an excellent method for desulfurization of mercaptans 9 to the corresponding hydrocarbons. Both reactions are essentially quantitative and occur under mild conditions. This alternative to the Raney nickel reduction may be attractive particularly when the mercaptan to be desulfurized bears other reducible groups (e.g., aliphatic ketones, olefins, benzylic alcohols).[9] We have found that desulfurization of 3 by triorganotin hydride is generally a faster process than reduction of the functionalities mentioned above.

The tremendous enhancement of the alkyl C–S bond reduction in compounds **3a–g** implies, to us, an interaction between tin and sulfur which further "softens" the sulfur. This labilizes that bond toward attack by the soft tributylstannyl radical relative to the C–S bonds in dialkyl sulfides (cf. Table I). There exists, however, controversy in the literature as to the existence of any π-character in the Sn–S bond. Data from ^1H NMR spectra of compounds of the type $R_3SnSSnR_3$ have been interpreted to mean that there is little, if any.[10] Infrared and Raman studies also on bis(triorganotin) sulfides led the authors to conclude that there was no π-contribution to the Sn–S bond.[11,12] In contrast to these, atomic susceptibility measurements on several organotin sulfides seem to indicate a definite degree of π-bonding.[10]

Table IV. Reduction of Phenyl Alkyl Sulfides 10 by 1 equiv of Tri-*n*-butyltin Hydride[a]

	PhSR, R	reactn time, h	% unreacted 10[b]	products,[b] % yield RH, 6	$PhSSnBu_3$ (3h)
10a	CH_2Ph	0.25	0	100	100 (89)
10b	t-C_4H_9	0.8	0	[c]	100 (62)
10c	i-C_3H_7	110	0	[c]	100 (95)
10d	c-C_6H_{11}	72	20	67	80
10e	C_2H_5	65	65	[c]	35
10f	CH_3	65	100	0	0

[a] Reaction conducted in refluxing benzene, using 2,2′-asobis(isobutyronitrile) as initiator. [b] NMR yield (isolated yield). [c] Gaseous product not analyzed.

A more general scheme can now be formulated which describes the reduction of dialkyl sulfides (Table I), benzylic sulfides (Table II), and other sulfides to be presented later in this paper. This involves a coupling at the processes outlined in eq 1 and 5. Reduction by TBTH occurs initially as the R^1–S bond (where R^1 can form the more stable carbon radical intermediate) in sulfide 1 selectively, if not specifically, to yield hydrocarbon 4 and tributylstannyl alkyl sulfide 3, eq 1. However, this specificity can be negated by the enhanced reactivity toward reduction by TBTH which the C–S bond in 3 exhibits, producing hydrocarbon 6 and bis(tributyltin) sulfide, eq 5. The degree of selectivity in desulfurization is determined by the competition between unsymmetric sulfide 1 and alkyl organotin sulfide 3 for tri-*n*-butyltin hydride.

Phenyl Sulfides. Since radical attack at sulfur in 3 was enhanced, possibly by the softening effect of the adjacent trialkylstannyl group, we next investigated the reduction of a set of phenyl alkyl sulfides, eq 7. Due to the delo-

$$Bu_3SnH + \underset{\mathbf{10}}{PhSR} \rightarrow \underset{\mathbf{6}}{RH} + PhSSnBu_3 \qquad (7)$$

calization possibilities of the sulfur lone pairs into the π-system of the adjacent phenyl ring, we anticipated a certain increase in reactivity of these sulfides toward TBTH relative to the dialkyl sulfides in Table I. Indeed, the data for the reduction of the alkyl C–S bond in phenyl sulfides 10, Table IV, reveals such an effect. Compounds 10 are more reactive toward tributyltin hydride than are the dialkyl sulfides, yet less so than alkyl tributylstannyl sulfides 3.

The phenyl sulfides **10a–e** exhibited greater reactivity toward TBTH relative to the corresponding methyl sulfides **1a–d** in Table I and **7a** in Table II, and the reductions were specific. However, the reaction times were none the less very long for phenyl sulfides **10c–e**, where the reducible C–S bond was to either a primary or secondary alkyl

(6) Mehrotra, R. C.; Gupta, V. D.; Sukhani, D. *Ind. J. Chem. F* **1969**, 708.

(7) The free radical reduction of the alkyl tributyltin sulfides 3 by TBTH to hydrocarbons and bis(trialkyltin) sulfides contrasts with the polar reaction of these reagents: Noltes and Creemers observed only exchange of organotin groups when butyl triethyltin sulfide was reacted with triphenyltin hydride: Creemers, H. M. J. C.; Noltes, J. G. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 1589. Creemers, H. M. J. C.; Verbeek, F.; Noltes, J. G. *J. Organomet. Chem.* **1967**, *8*, 469.

(8) An equimolar mixture of t-$C_4H_9SCH_2Ph$ (**7f**) and t-$C_4H_9SSnBu_3$ (**3b**) was reacted competitively with 1 equiv of TBTH. The hydride was consumed exclusively by **3b**, as measured (NMR) by its complete disappearance and persistence of all of **7f**.

(9) Pettit, G. R.; Van Tamlen, E. E. *Org. React.* (*N.Y.*) **1962**, *12*, 356.

(10) Schumann, H.; Schumann-Ruidisch, I.; Schmidt, M. In "Organotin Compounds"; Sawyer, A. K., Ed.; Marcel Dekker: New York, 1971; Vol. II, p 302.

(11) Kriegsmann, H.; Hoffmann, H.; Geissler, H. *Z. Anorg. Allg. Chem.* **1968**, *341*, 24.

(12) Marchand, A.; Mendelsohn, J.; Lebedeff, M.; Valade, J. *J. Organomet. Chem.* **1969**, *17*, 379.

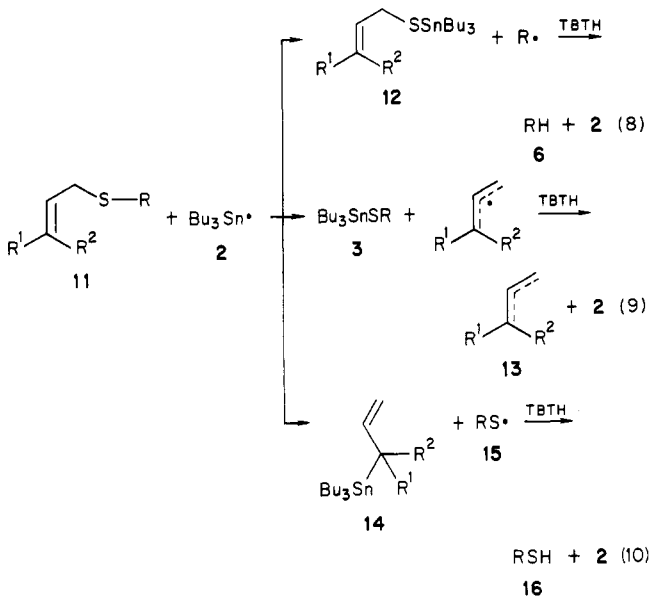
Table V. Reduction of Allylic Sulfides 11 by 1 equiv of Tri-*n*-butyltin Hydride[a]

allylic sulfides 11	reactn time, h	% unreacted[b] 11	products,[b,c] % yield: olefins 13	RH, 6	Bu_3SnSPh, 3	allyltin, 14	Bu_3Sn_2S
11a, $CH_3CH{=}CHCH_2SPh$	1	0	2-butene and 1-butene [2.5:1], 85	0	86	15	0
11b, 1-(phenylthio)cyclohex-2-ene	7	0	cyclohexene, 100	0	100 (76)	0	0
11c, $(CH_3)_2C{=}CHCH_2SPh$	2	0	2-methyl-2-butene and 3-methyl-1-butene [3:1], 97	0	100 (95)	0	0
11d, $CH_2{=}CHCH_2SCH_3$	20	10	*d*	*d*	(31)	(45)	
11e, $CH_3CH{=}CHCH_2SCH_3$	21	6	*d*	*d*	80	0	6
11f, 1-(methylthio)cyclohex-2-ene	25	2	cyclohexene, 98	*d*	86	0	12
11g, $(CH_3)_2C{=}CHCH_2SCH_3$	21	3	2-methyl-2-butene and 3-methyl-1-butene [3:1], 94	*d*	86	0	12
11h, $CH_3CH{=}CHCH_2SCH_2Ph$	1.2	50	2-butene and 1-butene, 50	CH_3Ph, 50	0	0	50
11i, 1-(benzylthio)cyclohex-2-ene	2.5	50	cyclohexene, 50	CH_3Ph, 50	0	0	50
11j, $(CH_3)_2C{=}CHCH_2SCH_2Ph$	1.3	50	2-methyl-2-butene and 3-methyl-1-butene, 50	CH_3Ph, 50	0	0	50

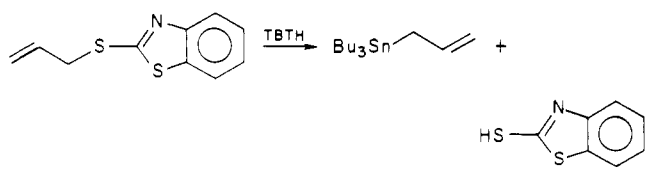
[a] Reaction done in refluxing benzene with AIBN initiation. [b] Determined by MR: integration of appropriate signals relative to diphenylmethane standard. [c] Values in parentheses are isolated yields. [d] Gaseous product not analyzed.

group.[13,14] This limits the synthetic utility of this procedure for such sulfides, particularly if other reducible functionality is present on these molecules.[3c] Methyl phenyl sulfide (**10f**) did not reduce at all.

Allylic Sulfides. The data for the equimolar reduction of allylic sulfides **11** with TBTH are reported in Table V. Tributylstannyl radical **2** can react with **11** in three possible primary substitution pathways: direct S_H substitution at sulfur (eq 8 and 9) or S_H' at the γ-carbon of the allyl



system (eq 10). Ueno and Okawara have reported the reaction of 2-(allylthio)-1,3-benzothiazole with twice the molar amount of TBTH to yield 88% of the allyltin product.[15]



Initially we sought to compare the competition between the S_H and S_H' processes in eq 9 and 10. To minimize the reaction outlined in eq 8 [and also the secondary reduction of tributylstannyl sulfide **3** by TBTH (cf. eq 5)], we first reacted phenyl allylic sulfides **11a–c** with 1 equiv of TBTH.

The major mode of TBTH reduction of crotyl phenyl sulfide (**11a**) was the S_H process, eq 9, evidenced not only by the formation of phenyl tributyltin sulfide (**3h**) as the major nonvolatile product but also by the trapping of a volatile mixture of both 1-butene and 2-butenes (2.5:1). The volatiles were analyzed by integrating the ^1H NMR signal (in CCl_4 solvent) of the methyl group in 2-butene (δ = 1.72 ppm) and the methyl triplet of 1-butene (δ = 1.04 ppm) relative to diphenylmethane standard. The S_H' reaction also occurs to a limited extent as indicated by the isolation of a 15% yield of (1-methylallyl)tributyltin and by the presence of thiophenol in the reaction mixture.

The reduction of 1-(phenylthio)cyclohex-2-ene (**11b**) and also of γ,γ-dimethylallyl phenyl sulfide (**11c**) proceeded specifically by the S_H process of eq 9, producing essentially quantitative amounts of cyclohexene in the first case and a mixture of 2-methyl-2-butene and 3-methyl-1-butene (3:1) in the second. In addition, no thiophenol (or its disulfide) was detected. Neither olefinic nor allylic ^1H NMR signals were detected (expected if allyltin products **14** were present) after the volatiles were removed. The only nonvolatile product was phenyl tributyltin sulfide (**3h**).

The S_H mode of reduction predominates (to the exclusion of the S_H' process) in the TBTH reduction of these allyl phenyl sulfides as substitution on the γ-carbon increases. Other investigations bear on these results. Terminal olefins undergo hydrostannation under free radical conditions.[16] However, the hydrostannation of nonterminal alkenes is sluggish at best.[17]

The S_H' process (eq 10) should also depend on the stability of the expelled sulfur radical **15**. In the work of Ueno and Okawara, and in the present reductions of phenyl allylic sulfides **11a–c**, the sulfur radicals formed could be

(13) Several authors report no reduction of such phenyl alkyl sulfides by triorganotin hydrides. These processes are described as uninitiated: (a) Clive, D. L. J.; Chittattu, G.; Wong, C. K. *J. Chem. Soc., Chem. Commun.* **1978**, 41. (b) Clive, D. L. J.; Chittattu, G. J.; Farina, V.; Kiel, W. A.; Menchen, S. M.; Russell, C. G.; Singh, A.; Wong, C. K.; Curtis, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 4438. (c) Brown, H. C.; Liu, K. T. *J. Am. Chem. Soc.* **1970**, *92*, 3502.

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Table VI. Reduction of α-(Alkylthio)- or α-(Arylthio)carbonyl Compounds by 1 equiv of Tri-n-butyltin Hydride[a]

	$RSCH_2R^1$		reactn time,	% unreacted	products,[b,c] % yield			
	R	R^1	min	17	CH_3R^1, 18	RH, 6	$RSSnBu_3$, 3	$(Bu_3Sn)_2S$
17a	CH_3	CN	5	0	*d*	0	100 (94)	0
17b	CH_3	$CO_2C_2H_5$	10	0	100	0	100 (91)	0
17c	n-C_6H_{13}	CO_2CH_3	25	6	94	*d*	88	*e*
17d	C_2H_5	$COCH_3$	15	3	*d*	*e*	95	*e*
17e	C_2H_5	COPh	4	0	100	0	100	0
17f	$PhCH_2$	COPh	5	8	92	8	84	8
17g	$PhCH_2$	CN	5	40	59	38	10	50
17h	$PhCH_2$	$COCH_3$	11	48	51	48	2	50
17i	$PhCH_2$	CO_2CH_3	10	50	50	50	0	50
17j	Ph	CN	3	0	*d*	0	100 (94)	0
17k	Ph	$COCH_3$	5	0	*d*	0	100 (94)	0
17l	Ph	CO_2CH_3	8	0	100	0	100 (93)	0
17m	*p*-ClPh	CN	10	0	*d*	0	100	0
17n	*p*-ClPh	$COCH_3$	11	0	*d*	0	100	0

[a] Reaction conducted in refluxing benzene using AIBN initiation. [b] Determined by NMR analysis: integration of appropriate signals of starting materials and/or products relative to the diphenylmethane internal standard. [c] Values in parentheses are isolated yields. [d] NMR signals were buried beneath the methylene envelope of $(C_4H_9)_3Sn$. [e] Not analyzed.

resonance stabilized. For comparison, we reacted allylic methyl sulfides **11d–g** each with 1 equiv of TBTH. Allyl methyl sulfide (**11d**) did react with TBTH in an S_H' manner to produce a 45% yield of tributylallyltin, considerably lower than the 88% yield observed by Ueno and Okawara in the reduction of 2-(allylthio)-1,3-benzothiazole.[15] We also found a 31% yield of methyl tributyltin sulfide, formed presumably by an S_H process, eq 9.

The presence of alkyl substituents on the γ-carbon of the allylic system of allylic methyl sulfides **11e–g** precluded any S_H' reaction. Instead these sulfides reacted extensively by the S_H process of eq 9. The final reaction mixtures can be accounted for by an initial specific cleavage of the allylic C–S bond in 11 followed by competition from methyl tributyltin sulfide (**3g**) for remaining TBTH. The initial allylic C–S bond homolysis was sluggish enough to allow slight competition by the slow reduction of CH_3SSnBu_3 (cf. Table III).

It is noteworthy that reduction of allylic phenyl sulfides **11a–c** was much faster (1–7 h) than that for allylic methyl sulfides **11d–g** (20–25 h). This reactivity enhancement parallels that observed earlier with other phenyl sulfides (cf. Table IV).

The benzyl C–S bond in benzyl methyl sulfide (**7a**) appears much more reactive toward TBTH than the allylic C–S bonds in sulfides **11d–f**, from the reaction times shown in Tables II and V. These results parallel those from polarographic reductions reported in the literature: benzylic C–S bonds reduce more readily than allylic C–S bonds.[18] We expected that reaction of TBTH with allyl benzyl sulfides **11h–j** would result in selective reduction of the benzylic C–S bond by eq 8. However, only half of the starting material was converted to toluene. Also, we found 50% yields each of olefins **13** and bis(tributyltin) sulfide. No allyl tributyltin mercaptolides **12** were observed. The relatively short reaction times suggest initial benzylic C–S bond homolysis. Indeed, these results can be accounted for by a scheme involving initial specific cleavage of the benzylic C–S bond (eq 8), followed by the very rapid consumption of remaining TBTH by the newly formed allyl tributyltin mercaptolide **12**, eq 5.

The reaction of 1-(benzylthio)cyclohex-2-ene (**11i**) with 2.2 equiv of TBTH has been reported. Schram and McIntosh observed 63% and 37% yields of toluene and cyclohexene, respectively, in this reduction.[19]

Carbonyl-Bearing Unsymmetric Sulfides. Manipulation of the carbonyl group plays a major role in organic synthesis. Consequently we investigated the behavior of TBTH toward thioethers in which carbonyl moieties are also present. TBTH is known to reduce carbonyl groups in aldehydes and ketones,[20] esters,[21] and acyl halides.[22]

α-(Methylthio)- and α-(Primary alkylthio)carbonyl Compounds. The results of the reaction of α-(methylthio or primary alkylthio)carbonyl compounds **17a–e** with 1 equiv of TBTH are presented in Table VI. As in the reduction of benzylic sulfides **7** and γ-substituted allylic sulfides **11**, these reactions can be described as occurring by initial specific cleavage of the α C–S bond in **17** (R^1 = carbonyl, cyano), followed by competition for TBTH by the generated organotin mercaptolide **3** (eq 5) and unreacted starting material **17** (eq 11). The very rapid re-

$$\underset{\mathbf{17}}{RSCH_2R^1} + Bu_3SnH \rightarrow \underset{\mathbf{18}}{CH_3R^1} + \mathbf{3} \qquad (11)$$

R^1 = carbonyl, CN

ductions of α-(methylthio)acetonitrile (**17a**) and ethyl α-(methylthio)acetate (**17b**) proceeded quantitatively and specifically at the α C–S bond. In these cases, the methyl tributyltin sulfide (**3a**) does not compete with starting sulfide for TBTH. Competition for TBTH from $RSSnBu_3$ **3** via eq 5 increases slightly as the R group in **17** (and consequently **3**) changes from methyl to primary alkyl, as indicated by the presence of small amounts of starting sulfide and $(Bu_3Sn)_2S$ in the final reaction mixtures.

The α C–S bond in α-(ethylthio)acetophenone (**17e**) was more reactive toward TBTH than was the α C–S bond in acetone derivative **17c**, the other ketone studied. The reduction of **17e** was quantitative and specific at the α C–S bond. In this case, the initial α C–S bond homolysis is rapid enough to completely overcome any competition by ethyl tributyltin sulfide (**3f**) for TBTH. The great reactivity toward TBTH of the α C–S bond in **17e** parallels an enhanced lability observed in the polarographic reduction of this bond[23] relative to C–S bonds α to other carbonyl groups.[18]

In addition to the observation that reduction of α C–S bonds in sulfides **17a–e** was extensive and rapid, we found that the carbonyl (and cyano) groups in these compounds

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Table VII. Competition between α-(to Carbonyl) C–S Bonds and Benzylic C–S Bonds for TBTH: Reaction of Equimolar Quantities of 17 and 7 with 1 equiv of TBTH[a]

competitors		% TBTH consumed by α C–S bond in 17[b]	% TBTH consumed by Bz C–S bond[b] in 7
$RSCH_2R^1$	$RSCH_2Ph$		
CH_3SCH_2CN (17a)	CH_3SCH_2Ph (7a)	86	14
$CH_3SCH_2CO_2C_2H_5$ (17b)	CH_3SCH_2Ph (7a)	60	40
n-$C_6H_{13}SCH_2CO_2CH_3$ (17c)	n-$C_6H_{13}SCH_2Ph$ (7c)	64	36
$C_2H_5SCH_2COCH_3$ (17d)	$C_2H_5SCH_2Ph$ (7b)	71	29
$C_2H_5SCH_2COPh$ (17e)	$C_2H_5SCH_2Ph$ (7b)	100	0

[a] Reaction run 20 min in refluxing benzene, with AIBN initiation. [b] Determined by NMR integration of appropriate signals of starting materials 17 and 7 and products toluene and methyl carbonyl compounds 18 relative to Ph_2CH_2 internal standard.

were inert toward the hydride under the reaction conditions used.

Competition Reactions between α-Carbonyl Sulfides $RSCH_2R^1$ (17) and Benzyl Alkyl Sulfides $RSCH_2Ph$ (7). We felt it useful to compare the reactivity of the α C–S bonds in $RSCH_2R^1$ (17) with that of benzylic C–S bonds in sulfides 7. We therefore reacted equimolar mixtures of sulfides 17 and 7 with 1 equiv of TBTH. The results of these studies, Table VII, reveal that in each case the α-(to carbonyl) C–S bond is more reactive toward TBTH than the benzylic C–S bond. These results correlate well with the polarographic reduction data for C–S bonds α-(to a carbonyl group) and of benzylic C–S bonds.[18]

α-(Benzylthio)carbonyl Compounds. The results of the reaction of 1 equiv of TBTH with α-(benzylthio)-carbonyl compounds **17f–i**, R = $PhCH_2$, are summarized in Table VI. TBTH selectively reduced α-(benzylthio)-acetophenone (**17f**) to produce largely acetophenone and benzyl tributyltin sulfide (**3a**) via eq 11, a result not unexpected in light of the electroreduction potentials reported for the two types of C–S bonds involved.[18,23]

In contrast, the TBTH reactions of **17g–i** all produced roughly equivalent amounts of carbonyl product **18** and toluene. If the only processes occurring were the direct cleavage of either the α C–S bond (eq 11) or the benzylic C–S bond (eq 12) of sulfide **17**, then the relative amounts

$$PhCH_2SCH_2R^1 + TBTH \rightarrow PhCH_3 + \underset{\mathbf{19}}{Bu_3SnSCH_2R^1} \quad (12)$$

of product carbonyl compounds **18** and toluene observed in these reductions should be similar to those observed in the analogous competition studies reported in Table VII. Since this is not the case, the involvement of secondary processes in the reductions of **17g–i** is suggested.

One of these secondary processes is likely to be the competitive consumption of TBTH by benzyl tributyltin sulfide (**3a**), via eq 5. In competition studies between equimolar quantities of **3a** and methyl α-(*n*-hexylthio)-acetate (**17c**) and between **3a** and α-(ethylthio)acetone (**17d**) (Table VI), we observed that the benzylic C–S bond in **3a** is reduced much more extensively than the α C–S bond. These results indicate that **3a**, produced by eq 11, can in fact compete with these starting α-(benzylthio)-carbonyl compounds for remaining TBTH.

The other probable secondary process is competitive consumption of TBTH by α-(carbonyl)tributyltin sulfides **19** (eq 13, one of the products of eq 12).

$$\underset{\mathbf{19}}{Bu_3SnSCH_2R^1} + TBTH \rightarrow \underset{\mathbf{18}}{CH_3R^1} + (Bu_3Sn)_2S \quad (13)$$

Compounds **19**, if indeed formed, must reduce very rapidly, since none of these are detected in the final TBTH reduction mixtures of sulfides **17f–i** (cf. Table VI). We prepared methyl α-[(tributylstannyl)thio]acetate (**19**, R^1 = CO_2CH_3) and treated it with 1 equiv of TBTH. This compound was reduced quantitatively to acetone and bis(tributyltin)sulfide in under 2 min.

α-(Phenylthio)carbonyl Compounds. α-(Phenylthio)carbonyl compounds **17j–n** were rapidly and specifically reduced to carbonyl (or nitrile) compounds **18** and aryl tributyltin sulfide **3h** quantitatively (Table VI). As in the reductions of phenyl alkyl sulfides **10** (cf. Table IV), we saw no cleavage of the aryl C–S bond. Also, the aryl C–Cl bond in α-(*p*-chlorophenylthio)carbonyls **17m** and **17n** is inert toward TBTH under the reaction conditions.[24]

Competition between C–S Bonds and Isolated Carbonyl Groups for TBTH. The α-(alkyl or arylthio)carbonyl compounds **17** in Table VI are readily reduced by TBTH at the α C–S bond presumably because of the intermediacy of a resonance-stabilized carbon radical adjacent to a carbonyl or nitrile function. To investigate the chemoselectivity of TBTH toward C–S bonds or carbonyl (or nitrile) functions isolated from each other, we performed several competition studies.

In the first series of experiments, benzyl methyl sulfide **7a** was allowed to compete with either dibenzyl ketone, pentyl acetate, or α-(1-naphthyl)acetonitrile for 1 equiv of TBTH. These reactions proceeded chemospecifically at the benzyl C–S bond. The TBTH was consumed in under 20 min in each case. No reduction of the carbonyl compounds was observed.

In the second series of competitions, isopropyl phenyl sulfide (**10c**) (whose C–S bond reduces slowly, cf. Table IV) was allowed to compete with an equimolar quantity of each of these same carbonyl compounds for 1 equiv of TBTH. Only the isopropyl C–S bond was reduced as though the carbonyl compounds were absent from the reaction mixtures. These reactions, which were stopped after 21 h, showed that the carbonyl compounds were inert toward TBTH over this reaction time under the conditions used. The isopropyl phenyl sulfide (**10c**) was reduced by TBTH to the same extent (35–40%) whether it had a carbonyl compound present or not.

Conclusion

Our studies indicate that the reaction between unsymmetric sulfides **1** and tri-*n*-butyltin hydride is best described as a coupling of the processes outlined in eq 1 and 5. Reduction by TBTH occurs initially at the R^1–S bond (where R^1 can form the more stable carbon radical inter-

(24) Higher temperatures than refluxing benzene are generally required to cleave aryl-halogen bonds with triorganotin hydrides: Rothman, L. A.; Becker, E. I. *J. Org. Chem.* **1959**, *24*, 294. Rothman, L. A.; Becker, E. I. *J. Org. Chem.* **1960**, *25*, 2203.

mediate) in sulfide 1 selectively, if not specifically, to yield hydrocarbons 4 and tributylstannyl alkyl sulfide 3, eq 1. However, this specificity can be negated by the enhanced reactivity toward reduction by TBTH which the C–S bond in 3 exhibits, producing hydrocarbon 6 and bis(tributyltin)sulfide, eq 5. The degree of selectivity in desulfurization is determined by the competition between unsymmetric sulfide 1 and alkyl organotin sulfide 3 for tri-*n*-butyltin hydride.

Thioether C–S bonds whose homolyses yield resonance-stabilized carbon radicals react extensively (and often rapidly) with TBTH. However, when homolysis yields localized carbon radicals, reduction of such C–S bonds is modest at best. In the cases where C–S bond cleavage would result in localized carbon radicals, the order of C–S bond reactivity toward TBTH paralleled the order of alkyl radical stabilities: 3° > 2° > 1° > methyl. However, in the TBTH reduction of sulfides 7, 11, and 17 (involving the intermediacy of resonance-stabilized carbon radicals), the order of reactivity of the C–S bonds was found to be α-(to carbonyl) > benzylic > γ-substituted allylic. These results are opposite those predicted based on the relative stabilities of the carbon radicals presumed to be involved.[25] However, the TBTH desulfurization results parallel closely the reactivities of these different C–S bonds toward polarographic reduction. This may be further evidence for the notion that the tributyltin radical is somewhat nucleophilic, relative to ordinary carbon radicals, and that polar character is developed in the transition state of these reactions.[26]

$$[C\cdots S\cdots SnBu_3]^{\delta^-\ \ \delta^+\ \ \ddagger}$$

Experimental Section

Boiling points were recorded at gauge pressure and are reported uncorrected. Nuclear magnetic resonance spectra were recorded on a Varian EM-390 spectrometer. Chemical shifts are reported in δ values relative to Me_4Si as standard. Quantitative NMR analyses were performed by electronic integration of the specific absorptions. At least three and generally four integrating scans were done. Where overlapping absorption signals were encountered, controls were run on weighed out mixtures for calibration purposes. NMR yields were determined by comparing the integrations of reaction products against an internal standard. Infrared spectra were recorded on either a Perkin-Elmer Infracord (using polystyrene calibration points) or a Beckman Accu-Lab 10. Analytical GLC was performed on a Beckman GC-45 instrument using a $^1/_8$ in. × 5 ft glass column packed with 5% OV-101 on Chromosorb W. Product yields from these analyses were determined by comparing integrations of the product peaks against an internal standard by applying appropriate flame factor corrections.

All reactions were run under a dry nitrogen atmosphere and were stirred magnetically.

Unsymmetric Sulfides. Compounds **1a–c**, **7a,b**, **10a,c,e,f**, **11e**, and **17a,b,d–m** were commercial samples. The purity of these was verified by ^{1}H NMR and IR, and, where required, the compounds were distilled prior to their use. Benzyl sulfides **7c–f** were prepared by the method of Shriner.[27] Phenyl sulfides **10b** and **10d** were obtained according to the procedures of Ipatieff[28] and of Zavgorodnii,[29] respectively. Alkyl (or aryl) tri-*n*-butyltin sulfides **3a,b,f–h** and methyl α-[(tributylstannyl)thio]acetate **19** (R^1 = CO_2CH_3)[30] were prepared as by Mehrotra.[6] Allylic sulfides **11a**,[31] **11b**,[32] **11c**,[33] **11f**,[32] and **11g**[34] were prepared by literature procedures. The synthesis of new alkyl tributyltin sulfides **3c–e** and of methyl α-(*n*-hexylthio)acetate (**17c**) are described below.

Isopropyl Tri-*n*-butyltin Sulfide (3c). A round-bottomed flask was charged with 7.02 g (11.78 mmol) of bis(tributyltin) oxide and 2.30 g (30.00 mmol) of isopropylmercaptan. The reaction mixture, which became cloudy immediately on mixing, was stirred 30 min. The material was diluted with 100 mL of pentane and washed sequentially with 5% NaOH, water, and brine and then dried over anhydrous sodium sulfate. Evaporation of the solvent gave 8.40 g (98%) of **3c** as colorless oil. Distillation gave analytically pure material: bp 110–13 °C (0.08 mm); ^{1}H NMR (CCl_4) δ 0.50–2.10 (m, 33 H, including a sharp doublet at 1.27), 2.95 (septet, 1 H); IR (neat on CsI plates) 391 cm^{-1} (Sn–S). Anal. Calcd for $C_{15}H_{34}SSn$: C, 49.33; H, 9.38; S, 8.78. Found: C, 49.31; H, 9.35; S, 8.81.

Cyclohexyl tri-*n*-butyltin sulfide (3d)[35] was similarly obtained as a colorless oil: bp 140–145 °C (0.1 mm); ^{1}H NMR (CCl_4) δ 0.40–2.21 (m, 37 H), 2.63 (m, 1 H); IR (neat on CsI) 387 cm^{-1} (Sn–S). Anal. Calcd for $C_{18}H_{38}SSn$: C, 53.35; H, 9.45; S, 7.91. Found: C, 53.37; H, 9.44; S, 7.95.

***n*-Hexyl tri-*n*-butyltin sulfide (3e)** was obtained as a colorless oil: bp 139–140 °C (0.03 mm); ^{1}H NMR (CCl_4) δ 0.25–2.15 (m, 38 H), 2.39 (t, 2 H); IR (neat on CsI) 345 cm^{-1} (SnS). Anal. Calcd for $C_{18}H_{40}SSn$: C, 53.09; H, 9.90; S, 7.87. Found: C, 53.10; H, 9.92; S, 7.81.

α-(*n*-Hexylthio)acetate (17c). A 250-mL round-bottomed flask was charged with 100 mL of anhydrous methanol and 1.60 g (70.0 mmol) of sodium shot. To the resulting alkoxide solution was added 7.12 g (67.1 mmol) of methyl thioglycolate. The mercaptide was stirred 30 min, and then 11.08 g (67.1 mmol) *n*-hexyl bromide was syringed dropwise into the reaction mixture. The material was stirred 2 h at room temperature and then refluxed for 2 h. The reaction mixture was transferred to a separatory funnel containing 250 mL of pentane. The organic solution was washed with 5% NaOH and water until neutral and then dried with brine and over anhydrous sodium sulfate. Filtration and evaporation of the solvent gave crude product which was fractionally distilled to yield 8.94 g (70%) of pure **17c**: bp 83–84 °C (1.6 mm); ^{1}H NMR (CCl_4/1% Me_4Si) δ 3.64 (s, 3 H), 3.08 (s, 2 H), 2.46–2.64 (t, 2 H), 0.73–1.79 (m, 11 H); IR (neat) 1745 cm^{-1} (C=O). Anal. Calcd for $C_9H_{18}O_2S$: C, 56.80; H, 9.53; S, 16.85. Found: C, 56.82; H, 9.50; S, 16.88.

General Procedure for Reduction of Unsymmetric Sulfides with Tri-*n*-butyltin Hydride.[36] Reductions were performed in an oven-dried (150 °C) 25-mL round-bottomed flask bearing a reflux condensor. The flask was charged with the sulfide, the appropriate amount of distilled benzene solvent (~0.6 mL/mmol sulfide), 1–2% recrystallized 2,2′-azobis(isobutyronitrile) (AIBN) as initiator, and 1.05–1.10 equiv of TBTH. The reaction flask was lowered into a preheated oil bath (~100 °C) so that benzene reflux was rapidly established. Aliquots were periodically withdrawn, the progress of the reaction was monitored by NMR (and/or GLC), and the aliquots were returned to the reaction flask. The reaction mixture was reinitiated with AIBN and the heating resumed. Analysis of the final reaction mixtures was done by NMR and/or GLC. The reaction mixtures were distilled where products were isolated.

Since all reductions are similar, only representative examples from each of the tables will be described.

Reduction of Methyl Cyclohexyl Sulfide (1b). Using the general procedure, 0.693 g (5.32 mmol) of **1b** and 1.702 g (5.85 mmol) of TBTH in 3 mL of benzene solvent were reacted in the presence of 20 mg of AIBN catalyst and 0.364 g (2.84 mmol) of

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(36) For convenient and inexpensive preparation of Bu_3SnH, see ref 4.

nonane as internal GLC standard. The mixture was refluxed for 24 h, analyzed by GLC and NMR, reinitiated with 2% AIBN, and refluxed an additional 26 h. GLC analysis of this final reaction mixture revealed the presence of 89% unreacted **1b**.

Reduction of *tert*-Butyl Methyl Sulfide (1d). The general procedure employed **1d** (0.575 g, 5.52 mmol), TBTH (1.08 g, 6.22 mmol), AIBN (21 mg), and diphenylmethane (1.053 g, 6.26 mmol) as internal standard, all dissolved in 3 mL of benzene. The mixture was refluxed for 15 h. NMR analysis at this time showed 60% unreacted starting materials. After reinitiation, reflux was continued for another 24 h. NMR analysis revealed that all of the TBTH [Bu_3SnH: δ_{PhH} = 4.55 ppm (s)] was consumed. The final reaction mixture consisted of CH_3SSnBu_3 [30% yield, δ_{PhH} = 1.67 ppm (s)], 33% unreacted **1d** [t-$C_4H_9SCH_3$ δ_{PhH} = 1.50 ppm (s)] and bis(tributyltin) sulfide.

Reduction of Benzyl *n*-Hexyl Sulfide (7c). Using the general procedure, a solution of 0.714 g (3.43 mmol) of **7c** in 2 mL of benzene was reacted with 1.047 g (3.60 mmol) of TBTH. AIBN (10 mg) was used as initiator. All TBTH was consumed after 30 min of reflux. The volatiles were removed in vacuo and trapped in a flask cooled in a dry ice–acetone bath. NMR analysis of the condensed volatiles (using diphenylmethane as standard) indicated an 84% yield of toluene and 16% of hexane. Similar analysis of the pot residue indicated a 68% yield of *n*-hexyl tri-*n*-butyltin sulfide (**3e**). Short-path distillation of the pot residue gave 0.796 g (57%) of **3e** which exhibited identical NMR and IR spectra with those of an authentic sample.

In a separate experiment, GLC analysis of the reaction products (using nonane as internal standard) revealed a 80% yield of toluene and 14% of hexane.

Reduction of Benzyl Tri-*n*-butyltin Sulfide (3a). By the general procedure 1.548 g (3.75 mmol) of **3a** in 2 mL of benzene was reduced with 1.116 g (4.01 mmol) TBTH. AIBN (10 mg) was used as initiator. The reaction was complete after 6 min of reflux. The volatile materials were removed in vacuo and condensed in a dry ice/acetone cooled trap. NMR analysis of this material (using diphenylmethane as internal standard) revealed a 95% yield of toluene. The pot residue was short-path distilled to give 2.044 g (89%) of bis(tributyltin) sulfide [bp 204–207 °C (20 mm)] which gave an infrared spectrum identical with that of an authentic sample.

Reduction of Isopropyl Phenyl Sulfide (10c). Following the general procedure, 0.842 g (5.53 mmol) of **10c** in 3 mL of benzene was reduced with 1.778 g (6.09 mmol) of TBTH, using 10 mg of AIBN as initiator. Reaction progress was monitored after 29, 53, 79, and 106 h. After 110 h the reaction was complete. The NMR spectrum showed the complete disappearance of both the Bu_3SnH signal as well as the methine signal in **10c** (a septet at δ = 2.8 ppm in PhH). The reaction mixture was evaporated and the residue short-path distilled to give 2.094 g (95%) of phenyl tributyltin sulfide: bp 152 °C (1.5 mm) [lit.[6] 137–144 °C (0.2 mm)]; NMR (CCl_4) δ 0.73–1.72 (m, 27 H), 7.00–7.52 (m, 5 H); IR (neat on CsI plates) 350 cm^{-1} (SnS stretch).

Reduction of 3-Methylbut-2-en-1-yl Phenyl Sulfide (11c). Using the general procedure, the starting mixture consisted of **11c** (1.049 g, 5.88 mmol), TBTH (1.902 g, 6.47 mmol), and 16 mg of AIBN in 2.5 mL of benzene. The reaction mixture was refluxed, and after 110 min, the starting materials were completely consumed. Removal of the volatiles under vacuum left 2.075 g (98%) of phenyl tributyltin sulfide (**3b**), whose NMR and IR data were identical with those of an authentic sample.

A separate experiment was done to determine the composition of the gaseous olefin products. In this procedure, another gas inlet was attached to the reaction vessel. The gas inlet on the condensor was attached to a U-tube trap cooled to −78 °C in a dry ice/acetone slush. The U-tube was connected to a gas bubbler filled with mineral oil. When the reaction mixture was refluxing, a slow but steady positive N_2 pressure was maintained to sweep the volatiles from the flask into the trap. After an hour of reflux, NMR analysis of the trapped volatiles showed a mixture of 2-methylbut-2-ene [CH_3CH=$C(CH_3)_2$ δ = 5.10 ppm (m); CH_3CH=$C(CH_3)_2$ δ = 1.61 ppm] and 3-methylbut-1-ene [$(CH_3)_2CHCH$=CH_2 δ = 5.55–6.00 ppm (m); $(CH_3)_2CHCH$=CH_2 δ = 4.72–5.10 ppm (m); $(CH_3)_2CHCH$=CH_2 δ = 2.25 ppm (m); $(CH_3)_2CHCH$=CH_2 δ = 0.96 ppm (d)] in a 76:24 ratio.

Reduction of α-(Methylthio)acetonitrile (17a). The general procedure employed TBTH (1.947 g, 6.69 mmol) and AIBN (28 mg) to reduce **17a** (0.530 g, 6.08 mmol) in 2.5 mL of benzene. The mixture was analyzed by NMR after 5 min of reflux. All of starting sulfide **17a** [CH_3SCH_2CN δ_{PhH} = 2.72 ppm (s); CH_3SCH_2CN δ_{PhH} = 1.57 ppm (s)] had been consumed. A quantitative production of CH_3SSnBu_3 (**3g**) [δ_{PhH} = 1.60 ppm (s)] was observed. The volatiles were then removed in vacuo, leaving 1.931 g (94%) of **3g**, whose NMR and IR data were identical with that of an authentic sample.

Competition between α-(Methylthio)acetonitrile (17a) and Benzyl Methyl Sulfide (7a). The general procedure used **17a** (0.534 g, 6.13 mmol), **7a** (0.857 g, 6.20 mmol), TBTH (1.895 g, 6.51 mmol), AIBN (25 mg), and diphenylmethane standard (0.570 g, 3.39 mmol) in 3.0 mL of benzene. The reaction mixture was refluxed for 20 min and then analyzed by NMR. This analysis, done by comparing integrations of the standard [Ph_2CH_2 δ_{PhH} = 3.43 ppm (s)] with the appropriate signals of starting materials **17a** [CH_3SCH_2CN δ_{PhH} = 2.72 ppm (s)] and **7a** [$PhCH_2SCH_3$ δ_{PhH} = 3.10 ppm (s)] and toluene product revealed that the reduction of **17a** consumed 86% of the TBTH, while that of **7a** used only 14% of the TBTH.

Reduction of Methyl α-[(Tributylstannyl)thio]acetate (19). Using the general reduction procedure, a mixture of **19** (1.259 g, 3.19 mmol), TBTH (1.020 g, 3.50 mmol), and AIBN (12 mg) in 2.0 mL of benzene was refluxed for 1.5 min. NMR analysis at this point revealed that starting materials were completely consumed (absence of Bu_3SnH [δ_{PhH} = 4.55 ppm (m)] and **19** [$Bu_3SnSCH_2CO_2CH_3$ δ_{PhH} = 3.01 ppm (s); $CH_3CO_2CH_3$ δ_{PhH} = 1.37 ppm (s)]). The volatiles were removed from the reaction mixture in vacuo. An infrared spectrum of the residue (1.941 g, 99%) was identical with that of authentic $(Bu_3Sn)_2S$.

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Registry No. **1a**, 20291-60-5; **1b**, 7133-37-1; **1c**, 1551-21-9; **1d**, 6163-64-0; **1e**, 14290-92-7; **1g**, 44657-76-3; **3a**, 23728-85-0; **3b**, 23728-82-7; **3c**, 79851-32-4; **3d**, 64495-81-4; **3e**, 93222-30-1; **3f**, 23716-85-0; **3g**, 17314-32-8; **3h**, 17314-33-9; **3m**, 24735-27-1; **7a**, 766-92-7; **7b**, 6263-62-3; **7c**, 34005-03-3; **7d**, 19843-98-2; **7e**, 770-34-3; **7f**, 7417-73-4; **10a**, 831-91-4; **10b**, 3019-19-0; **10c**, 3019-20-3; **10d**, 7570-92-5; **10e**, 622-38-8; **10f**, 100-68-5; **11a**, 702-04-5; **11b**, 3467-73-0; **11c**, 10276-04-7; **11d**, 10152-76-8; **11e**, 32931-14-9; **11f**, 34046-61-2; **11g**, 5897-45-0; **11h**, 31409-96-8; **11i**, 65539-52-8; **11j**, 880-22-8; **17a**, 35120-10-6; **17b**, 4455-13-4; **17c**, 93222-31-2; **17d**, 20996-62-7; **17e**, 10271-55-3; **17f**, 13402-51-2; **17g**, 17377-30-9; **17h**, 10230-69-0; **17i**, 17277-59-7; **17j**, 5219-61-4; **17k**, 5042-53-5; **17l**, 17277-58-6; **17m**, 18527-19-0; **17n**, 25784-83-2; **18b**, 141-78-6; **18c**, 79-20-9; **18e**, 98-86-2; **18g**, 75-05-8; **18h**, 67-64-1; **19**, 31614-63-8; TBTH, 688-73-3; AIBN, 78-67-1; $PhCH_3$, 108-88-3; c-C_6H_{12}, 110-82-7; n-C_6H_{14}, 110-54-3; CH_3CH=$CHCH_3$, 107-01-7; CH_2=$CHCH_2CH_3$, 106-98-9; c-C_6H_{10}, 110-83-8; $(CH_3)_2C$=$CHCH_3$, 513-35-9; $(CH_3)_2CHCH$=CH_2, 563-45-1; $Bu_3SnCH(CH_3)CH$=CH_2, 76505-19-6; Bu_3SnCH_2CH=CH_2, 24850-33-7; $(Bu_3Sn)_2O$, 56-35-9; $(Bu_3Sn)_2S$, 4808-30-4; i-C_3H_7SH, 75-33-2; c-$C_6H_{11}SH$, 1569-69-3; n-$C_6H_{13}SH$, 111-31-9; $HSCH_2CO_2Me$, 2365-48-2; n-$C_6H_{13}Br$, 111-25-1.