formed the chemical shift and ^{13}C NMR analyses.

Registry No. 1, 89-80-5; **3**-OH, 73908-31-3; **3**-OTs, 73908-32-4; **4**, 4789-24-6; **4a**, 73908-33-5; **6**-OH, 73908-34-6; **6**-OTs, 73908-35-7; **7**-Cl, 29707-60-6; **7**-OTs, 7212-65-9; **8**-Cl, 26348-39-0; **8**-OH, 491-01-0; **8**-OTs, 14539-76-5; **10**, 500-00-5; **10**-d_3, 73908-36-8; **11**, 5256-65-5; **12**-OH, 3239-03-0; **12**-OH-d_3, 73908-37-9; **12** ODNB, 73908-38-0; **13**-OH, 3239-02-9; **13**-OH-d_3, 73908-39-1; **14**, 1124-27-2; **14**-d_3, 73908-40-4; **15**, 19140-67-1; **15**-*d*, 62222-93-9; **15**-d_3, 62222-94-0; **16**-*d*, 62239-64-9; **16**-d_3, 62239-65-0; **17**-OTs, 57573-68-9; menthol, 1490-04-6; neoisomenthol, 491-02-1; 1-methyl-3-(*tert*-butylacetoxy)cyclohexane, 73908-41-5.

Tri-*n*-butyltin Hydride: A Selective Reducing Agent for 1,3-Dithiolanes

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Tri-*n*-butyltin hydride has been found to be an effective and selective agent for complete or partial desulfurization of 1,3-dithiolanes 1. The reaction of 1 with 4 equiv of tri-*n*-butyltin hydride in the presence of 2,2′-azobis(isobutyronitrile) results in complete desulfurization, giving hydrocarbons 2 in good yield, ethane, and bis(tri-*n*-butyltin) sulfide. Two equivalents of hydride specifically cleave the two geminal C–S bonds in 1 to give hydrocarbons 2 and bis(tri-*n*-butylstannyl) ethanedithiolate. One equivalent of tri-*n*-butyltin hydride reduces 1 quantitatively to the β-[alkyl(or aryl)thio]ethyl tri-*n*-butyltin sulfides 11.

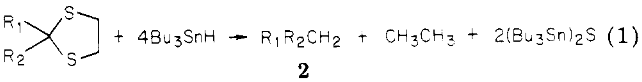
The hydrogenolysis of dithioacetals and dithioketals has been extensively utilized as an alternative to the Wolff–Kishner or Clemmensen reduction of the parent aldehyde or ketone. These desulfurizations have most commonly been achieved by the use of Raney nickel[1] or alkali metals in ammonia (or alkylamine) solution.[2] Reagents such as hydrazine,[3] cupric chloride–zinc chloride–lithium aluminum hydride,[4] and nickel boride[5] have also been used. While these procedures are excellent where complete desulfurization is desired, they do not generally allow for the selective reduction of one carbon–sulfur bond, leaving others in the same molecule intact.[6] We wish to report the use of tri-*n*-butyltin hydride as an effective and selective agent in the reduction of dithioketals and dithioacetals.

Table I. Reduction of 1,3-Dithiolanes 1 by 4 Equiv of Tri-*n*-butyltin Hydride[a]

ethylene thioketal or -acetal of	no.	hydrocarbon product 2	% isolated yield
cyclohexanone[b]	3	cyclohexane	76[e]
benzaldehyde[b]	4	toluene	73[e]
6-methoxy-α-tetralone[c]	5	6-methoxytetralin	95[e]
heptanal[b]	6	heptane	80[e]
10-methyl-$\Delta^{1,9}$-2-octalone[c,d]	7	10-methyl-$\Delta^{1,9}$-octalin[d] (8) and 10-methyl-$\Delta^{1,2}$-octalin (9)[g]	74[f]

[a] 2,2′-Azobis(isobutyronitrile) (1%) used as catalyst. [b] Reference 6. [c] Benzene used as reaction solvent. [d] Reference 13. [e] By short-path distillation into a cooled flask. [f] By column chromatography on silica gel. [g] In a 4.2:1 ratio, respectively.

Although there have appeared a limited number of studies wherein organotin hydrides have reduced an organosulfur functionality,[7] there was, at the start of this study, no clear indication which of the four carbon–sulfur bonds in dithiolanes 1, if any, would be cleaved by tri-*n*-butyltin hydride. Initially we attempted complete desulfurization of 1 to hydrocarbon 2 by using 4 equiv of the organotin hydride with the anticipation that the reaction represented by eq 1 would proceed.


$$+ 4Bu_3SnH \rightarrow R_1R_2CH_2 + CH_3CH_3 + 2(Bu_3Sn)_2S \quad (1)$$

1 **2**

Treatment of the ethylene dithioketal of cyclohexanone with 4 equiv of the organotin hydride did indeed produce some cyclohexane and bis(tri-*n*-butyltin) sulfide. Ethane was presumably also formed, but no attempts were made to trap it. The reaction was less than half complete after 39 h (as monitored by the disappearance of the SCH_2CH_2S ^1H NMR signal of starting material). However, the reaction was completed in less than 2 h upon addition of 1% azobis(isobutyronitrile) (AIBN) in a subsequent experiment. On the other hand, the presence of hydroquinone or galvinoxyl inhibited the reduction. The above experiments suggest free-radical intermediates, the involvement of which is well documented in many organotin hydride reactions.[8]

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Table II. Reduction of 1,3-Dithiolanes 1 with 1 Equiv of Tri-*n*-butyltin Hydride

starting material	product
3	$C_6H_{11}SCH_2CH_2SSnBu_3$ (13)
4	$PhCH_2SCH_2CH_2SSnBu_3$ (14)
5	(6-MeO-α-Tet)$SCH_2CH_2SSnBu_3$[a] (15)
6	$CH_3(CH_2)_6SCH_2CH_2SSnBu_3$ (16)

[a] Tet = tetralyl.

Table III. Destannylation of β-[Alkyl(or aryl)thio]ethyl Tributyltin Sulfides 11 on Silica Gel

starting material	product 12	isolated yield, %
13	$C_6H_{11}SCH_2CH_2SH$[a] (17)	64
14	$PhCH_2SCH_2CH_2SH$ (18)	82
15	(6-MeO-α-Tet)SCH_2CH_2SH[b] (19)	75
16	$CH_3(CH_2)_6SCH_2CH_2SH$[a] (20)	72

[a] Reference 6. [b] Tet = tetralyl.

To test the generality of this desulfurization procedure, we reduced a set of 1,3-dithiolanes 1 as above to give the corresponding hydrocarbons 2 and bis(tri-*n*-butyltin) sulfide (and presumably ethane). The results are summarized in Table I. Mixtures of neat reagents were employed when they were soluble in each other. In cases where the dithiolanes were solid and not readily soluble in tri-*n*-butyltin hydride, the reactions were run in benzene solution.[9]

The reductions gave the expected hydrocarbon products in good yield. Noteworthy is the reduction of allylic dithiolane 7, which gave not only the desired olefin 8 but also isomeric 9 in a 4.2:1 mixture. Organotin hydride reduction of other allylic functions have at times been complicated by production of isomeric olefinic products.[10]

When 1,3-dithiolanes 3–5 and 7 were each reacted with only 2 equiv of tri-*n*-butyltin hydride, we observed the formation of the same hydrocarbon products 2 in yields similar to those obtained when 4 equiv of the reducing agent was used. The other major product was bis(tributylstannyl) ethanedithiolate[11] (10, eq 2). However, when

$$1 + 2Bu_3SnH \xrightarrow{AIBN} 2 + \underset{\textbf{10}}{Bu_3SnSCH_2CH_2SSnBu_3} \qquad (2)$$

the heptanal ethylene dithioacetal, 6, was reacted with only 2 equiv of tri-*n*-butyltin hydride, the product consisted of a complex mixture containing bis(tri-*n*-butyltin) sulfide, heptyl tri-*n*-butyltin sulfide, heptane, and ethyl heptyl sulfide.

When 1 equiv of tri-*n*-butyltin hydride was reacted with 1 equiv of 1,3-dithiolanes 1, we observed the selective cleavage of only one C–S bond, leading to the β-[alkyl(or aryl)thio]ethyl tri-*n*-butyltin sulfides 11 (eq 3). These results are summarized in Table II.

$$1 + Bu_3SnH \xrightarrow{AIBN} \begin{array}{l} R_1R_2CHSCH_2CH_2SR_3 \\ \textbf{11}, R_3 = SnBu_3 \\ \textbf{12}, R_3 = H \end{array} \qquad (3)$$

The yields of compounds 11 were essentially quantitative. However, our attempts to purify them for analyses were not successful. Distillation of these oils at reduced pressure or chromatography on Florisil, silica gel, or alumina resulted in considerable decomposition. Of interest is that silica gel effected complete destannylation of compounds 11 to β-[alkyl(or aryl)thio]ethyl mercaptans 12 on attempted chromatography [bis(tri-*n*-butyltin) oxide was also isolated] (Table III).

Similar selective reduction of 1,3-dithiolanes 1 directly to β-(alkylthio)ethyl mercaptans 12 has previously been achieved by Eliel and co-workers by using controlled amounts of calcium in liquid ammonia.[6,12] The present procedure offers the synthetic advantage of selective C–S bond cleavage in 2-aryldithiolanes of types 4 and 5 to compounds 14 and 15. In the dissolving metal reduction studies mentioned, the authors were unable to prevent complete desulfurization of 2-phenyl-1,3-dithiolane 4 to toluene, ethanedithiol, and other products since the conditions are known to cleave benzyl sulfides to hydrocarbons.[6]

A reaction scheme consistent with the data obtained from the reaction of 1 with 1, 2, or 4 equiv of tri-*n*-butyltin hydride is shown in eq 4–7. Only chain propagation is shown.

$$Bu_3Sn\cdot + 1 \rightarrow \underset{\textbf{21}}{R_1R_2\dot{C}SCH_2CH_2SSnBu_3} \qquad (4)$$

$$\textbf{21} + Bu_3SnH \rightarrow \textbf{11} + Bu_3Sn\cdot \qquad (5)$$

$$Bu_3Sn\cdot + \textbf{11} \rightarrow \underset{\textbf{22}}{R_1R_2\dot{C}H} + \textbf{10} \qquad (6)$$

$$\textbf{22} + Bu_3SnH \rightarrow \textbf{2} + Bu_3Sn\cdot \qquad (7)$$

The selectivity shown by the organotin hydride in the reduction of the various C–S bonds in 1,3-dithiolanes 1 can be accounted for by the different stabilities of the free-radical intermediates involved. Initial attack by tri-*n*-butyltin radical on 1 would cleave a C–S bond leading to intermediate 21 (eq 4). This radical should be relatively stable due to its proximity to a sulfur atom and the delocalization possibilities of the lone electron into empty sulfur d orbitals. Hydrogen atom transfer would produce sulfides 11 (eq 5). The cleavage of the second C–S bond involves the intermediacy of radical 22, clearly a less stable species than 21. Hydrogen atom transfer to 22 gives hydrocarbons 2.

That compounds 11 can be produced from the reaction of 1 equiv each of tri-*n*-butyltin hydride and 1 without overreduction to hydrocarbon 2 implies that eq 4, wherein the first C–S bond is ruptured, leading to radical intermediate 21, represents a much faster process than does eq 6, the cleavage of the second C–S bond via radical 22. The reduction of the remaining two C–S bonds in the conversion of bis(tributylstannyl) ethanedithiolate (10) to ethane and bis(tri-*n*-butyltin) sulfide (using the third and fourth equivalents of organotin hydride) involves the intermediacy of primary radicals. Consequently, these are much slower processes than even that represented by eq 6.

The observation that treatment of heptanal dithioacetal 6 with 2 equiv of reducing agent gave a complex mixture of products can be explained as follows: 6 reacted with the first equivalent of tri-*n*-butyltin hydride to β-(heptylthio)ethyl tri-*n*-butyltin sulfide (16). Reaction of 16 with the second equivalent of hydride is complicated by the fact that the cleavage of every remaining C–S bond involves

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(8) For a review on the reduction of organic compounds by organotin hydrides, see H. G. Kuivila, *Synthesis*, 499 (1970).

(9) It was observed that the reactions proceeded at a faster rate in benzene solution even if the reagents were soluble in each other. This may be due to greater solubility of AIBN in benzene than in the tri-*n*-butyltin hydride/1,3-dithiolane mixture.

(10) For an example, see L. A. Paquette, G. H. Birnberg, J. Clardy, and B. Parkinson, *J. Chem. Soc., Chem. Commun.*, 129 (1973).

(11) S. Sakai, H. Niimi, and Y. Ishi, *J. Organomet. Chem.*, 72, 103 (1974).

(12) E. L. Eliel, T. W. Doyle, R. A. Daignault, and B. C. Newman, *J. Am. Chem. Soc.*, 88, 1828 (1966).

the intermediacy of primary radicals. Consequently, the process is not very discriminating and leads to the observed mixture of products.

In conclusion, tri-*n*-butyltin hydride has been shown to be a selective agent for partial or complete hydrogenolysis of 1,3-dithiolanes. That it can cleave and discriminate between primary, secondary and benzylic C–S bonds implies that it may well be a general yet selective (when the stoichiometry is controlled) desulfurization agent.

Experimental Section

Melting points are reported uncorrected. Boiling points were recorded at gauge pressure and are reported uncorrected. GLC purifications were performed on a Varian Aerograph Model 90-P gas chromatograph with 3% OV-17 on Chromosorb W in a $^1/_4$ in. × 10 ft aluminum column. Nuclear magnetic resonance spectra were recorded on either a Varian EM-360 or EM-390 spectrometer. Chemical shifts are reported in δ values relative to tetramethylsilane as internal standard. Infrared spectra were recorded on a Perkin-Elmer Infracord, using polystyrene calibration points. Only selected absorptions are reported. High-resolution mass spectra were determined on a Varian M-60 instrument. All reactions were run under a dry nitrogen atmosphere.

Synthesis of 1,3-Dithiolanes. The 1,3-dithiolanes **3**, **4**, and **6** were prepared by the method of Eliel and Newman,[6] and **7** was prepared according to Sondheimer and Rosenthal.[13] Compound **5**, the only new 1,3-dithiolane, was prepared as follows. To a 0 °C solution of 10.00 g (0.057 mol) of 6-methoxy-α-tetralone and 8.50 g (0.092 mol) of 1,2-ethanedithiol in 50 mL of dichloromethane was added 2 mL of boron trifluoride etherate dropwise. The reaction mixture was stirred 20 min, warmed to room temperature, and stirred an additional 2 h. The material was washed sequentially with 5% NaOH, water, and brine and then dried over anhydrous sodium sulfate. Removal of the solvent gave 12.76 g (89%) of white crystalline **5**. An analytical sample was recrystallized from petroleum ether (bp 35–60 °C): mp 81–82 °C; ^{1}H NMR (CCl_4) δ 1.70–2.46 (m, 4 H), 2.79 (br t, 2 H), 3.38 (m, 4 H), 3.69 (s, 3 H), 6.28–7.90 (m, 3 H); high-resolution mass spectrum, calcd for $C_{13}H_{16}OS_2$ m/e 252.0643, found 252.0620.

General Reduction Procedure. Reductions were generally performed on 12 mmol of 1,3-dithiolanes **1** in a flame-dried, round-bottomed flask equipped with a reflux condenser. To the flask was added 4 or 2 or 1 equiv of tri-*n*-butyltin hydride,[14] as required, and azobis(isobutyronitrile) as catalyst. Solvent was added if necessary (see Table I). The reaction flask was warmed to 80 °C in an oil bath. Aliquots were periodically withdrawn, analyzed by NMR, and returned to the reaction vessel. Progress was monitored by the disappearance of the Bu_3SnH signal and the SCH_2CH_2S signal of reactant 1,3-dithiolane and the appearance of product signals. On reaching completion, the reaction mixture was short-path distilled. Alternatively, where distillation was not practical (e.g., reduction of **7**), the reaction solvent was evaporated and the residue chromatographed on silica gel.

Since the reductions performed are all similar, only the reactions of the ethylene dithioketal of cyclohexanone,[6] **3**, with 4, 2, or 1 equiv of tri-*n*-butyltin hydride will be described as specific examples.

Reduction of 3 with 4 Equiv of Tri-*n*-butyltin Hydride. To a stirred solution of 2.09 g (0.012 mol) of cyclohexanone ethylene dithioketal (**3**) and 13.97 g (0.048 mol) of tri-*n*-butyltin hydride was added 80 mg of recently recrystallized azobis(isobutyronitrile). The reaction mixture was reacted at 80 °C for 1.5 h and then short-path distilled at house vacuum pressures (90–160 mm). The volatile material was trapped in a receiving flask cooled in a dry ice-acetone bath, yielding 0.79 g (76%) of cyclohexane which gave NMR and IR spectra identical with an authentic sample. The pot residue was further distilled at reduced pressure to give 4.55 g (62%) of bis(tri-*n*-butyltin) sulfide [bp 204–206 °C (20 min)] which gave an infrared spectrum identical with an authentic sample.

Reduction of 3 with 2 Equiv of Tri-*n*-butyltin Hydride. To a solution of 1.92 g (0.011 mol) of **3** and 6.40 g (0.022 mol) of tri-*n*-butyltin hydride was added 40 mg of azobis(isobutyronitrile), and the mixture was then warmed to 80 °C. The reaction was complete in 1.1 h as indicated by the disappearance of the SCH_2CH_2S ^{1}H NMR signal of starting dithiolane at δ 3.27 (relative to external Me_4Si) and the appearance of a new sharp signal at δ 2.18 from ethanedithiolate product **10**. Short-path distillation at house vacuum pressures as before gave 0.63 g (68%) of cyclohexane identical with an authentic sample. Continued distillation under reduced pressure (vacuum pump) gave 3.92 g (53%) of bis(tri-*n*-butylstannyl) ethanedithiolate, bp 208–215 °C (0.4 mm). This material was identical with a sample prepared according to Sakai, Niimi, and Ishi.[11]

Reduction of 3 with 1 Equiv of Tri-*n*-butyltin Hydride. A mixture of 2.08 g (0.012 mol) of **3** and 3.49 g (0.012 mol) of tri-*n*-butyltin hydride was reacted at 80 °C in the presence of 20 mg of azobis(isobutyronitrile). The reaction was complete after 1.5 h. The NMR (CCl_4) was consistent with the formation of β-(cyclohexylthio)ethyl tri-*n*-butyltin sulfide (**13**): δ 2.62 (m, 1 H), 2.54 (s, 4 H), 2.02–0.81 (m, 37 H). Attempts at purification by distillation at reduced pressure or by column chromatography on a variety of adsorbants was accomplished by extensive decomposition.

Destannylation of 13 to β-(Cyclohexylthio)ethyl Mercaptan (17). A 4.02-g (8.6 mmol) sample of **13** was adsorbed on a column containing 80 g of silica gel. Elution with pentane–dichloromethane mixtures gave 0.69 g of bis(tri-*n*-butyltin) oxide (27%) followed by 0.97 g (64%) of β-(cyclohexylthio)ethyl mercaptan (**17**): bp 82–84 °C (0.5 mm) [lit.[6] bp 85 °C (0.6 mm)]. This product gave NMR and IR spectra identical with an authentic sample prepared according to Eliel and Newman.[6]

β-(Benzylthio)ethyl tri-*n*-butyltin sulfide (14) was obtained as a colorless oil: ^{1}H NMR (CCl_4) δ 0.30–2.03 (m, 27 H), 2.53 (m, 4 H), 3.67 (s, 2 H), 7.28 (s, 5 H).

β-[(6-Methoxy-α-tetralyl)thio]ethyl tri-*n*-butyltin sulfide (15) was obtained as a colorless oil: ^{1}H NMR (CCl_4) δ 0.63–2.20 (m, 33 H), 2.43–2.88 (m, 6 H, including a sharp singlet at 2.60), 3.68 (s, 3 H), 4.03 (m, 1 H), 6.29–7.36 (m, 3 H).

β-(Heptylthio)ethyl tri-*n*-butyltin sulfide (16) was obtained as a colorless oil: ^{1}H NMR (CCl_4) δ 0.50–2.08 (m, 40 H), 2.31–2.80 (m, 6 H, including a sharp singlet at 2.62).

β-(Benzylthio)ethyl Mercaptan (18) was obtained as a colorless oil: ^{1}H NMR (CCl_4) δ 1.50 (m, 1 H), 2.54 (m, 4 H), 3.64 (s, 2 H), 7.25 (s, 5 H); IR (neat) 2530 cm^{-1}; high-resolution mass spectrum, calcd for $C_9H_{12}S_2$ m/e 184.0380, found 184.0395.

β-[(6-Methoxy-α-tetralyl)thio]ethyl Mercaptan (19) was obtained as a colorless oil: ^{1}H NMR (CCl_4) δ 1.52 (m, 1 H), 1.80–2.21 (m, 4 H), 2.54–2.96 (m, 6 H), 3.81 (s, 3 H), 4.04 (m, 1 H), 6.25–7.33 (m, 3 H); IR (neat) 2540 cm^{-1}; high-resolution mass spectrum, calcd for $C_{13}H_{18}OS_2$ m/e 254.0799, found 254.0787.

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Registry No. 3, 177-16-2; **4**, 5616-55-7; **5**, 73622-41-0; **6**, 6008-84-0; **7**, 73622-42-1; **8**, 13943-77-6; **9**, 73622-43-2; **10**, 35525-50-9; **13**, 73622-44-3; **14**, 73622-45-4; **15**, 73622-46-5; **16**, 73622-47-6; **17**, 10160-81-3; **18**, 69078-70-2; **19**, 73622-48-7; **20**, 26718-05-8; cyclohexane, 110-82-7; toluene, 108-88-3; 6-methoxytetralin, 1730-48-9; heptane, 142-82-5; 6-methoxy-α-tetralone, 1078-19-9; 1,2-ethanedithiol, 540-63-6; tri-*n*-butyltin hydride, 688-73-3; bis(tri-*n*-butyltin) sulfide, 4808-30-4; bis(tri-*n*-butyltin) oxide, 56-35-9.

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(15) This study was presented in part at the American Chemical Society/Chemical Society of Japan Chemical Congress, Honolulu, HI, Apr 1979, abstract ORGN 460.