rically. The reaction was stopped when two or more analyses indicated that no more hydride was taken up. The solutions were transferred by means of a hypodermic syringe. For reaction of compounds with active hydrogen, the reaction flask was attached to a gas meter.

The reduction of anthraquinone is described here as a representative procedure. After a 30-min reaction time at 0 °C, hydrolysis of a 4-mL aliquot of the reaction mixture indicated 2.83 mmol of residual hydride, which means 1.17 mmol of hydride per mol of anthraquinone had been consumed. After 24 h, the analysis showed 1.98 mmol of residual hydride (after correction for hydrogen evolution), which indicated 2.02 mmol of hydride per mol of the compound had been consumed.

General Procedure for Stereoselective Study. The reduction of 2-methylcyclohexanone is representative. To a 100-mL, round-bottomed flask fitted with a side arm and capped by a rubber septum was added a 2.0-mL solution of KIPBH in THF (3.12 mmol in hydride). The flask was kept at 0 °C with the aid of an ice bath. To this was added 1.0 mL of a 2-methylcyclohexanone solution in THF (1.56 *M* in ketone). The reaction mixture was kept at 0 °C for 3 h (3 days at −25 °C). It was then hydrolyzed by addition of 2 mL of 2 *N* HCl solution. The aqueous layer was saturated with anhydrous potassium carbonate, and the organic layer was analyzed by GC. The results are summarized in Table III.

General Procedure for Stepwise Hydroboration with Haloboranes. The reaction of *n*-octylthexylchloroborane is representative. A 100-mL, round-bottomed flask equipped with a nitrogen inlet and a magnetic stirring bar was charged at 0 °C with 1.0 mL of *n*-dodecane (0.75 g, 4.40 mmol), the internal standard, and 1.57 mL of 1-octene (1.12 g, 10.0 mmol). Then 5.0 mL of 2.0 *M* cold thexylchloroborane methyl sulfide (10.0 mmol) in CH_2Cl_2 was added. After 5 min at 0 °C, the ice bath was replaced with a water bath and the mixture was stirred at 25 °C for 1 h. After cooling to 0 °C, 1.90 mL of 1-decene (1.40 g, 10.0 mmol) was added. Then 6.41 mL of 1.56 *M* KIPBH (>99% purity) in THF was added dropwise by using a syringe over a 3–5-min period. A white precipitate was formed immediately. The resulting mixture was stirred for 1 h at 0 °C and then oxidized by adding 10 mL of THF, 12 mL of 6 *N* NaOH, 10 mL of absolute ethanol, and 6 mL of 30% aqueous hydrogen peroxide (dropwise). After being stirred at 0 °C for 1 h, the mixture was heated at 55 °C overnight and cooled to room temperature. Absolute Et_2O (10 mL) was added and the aqueous layer was saturated with anhydrous potassium carbonate. GC analysis of the organic layer showed the formation of 10.0 mmol of 1-decanol. The results are summarized in Table XII. A full experimental section for carbonylation and cyanidation reactions has been described elsewhere.[16]

Registry No. KIPBH, 42278-67-1; KH, 7693-26-7; $(i\text{-PrO})_3B$, 5419-55-6; $K(i\text{-PrO})_4B$, 84581-08-8; 1-hexanol, 111-27-3; benzyl alcohol, 100-51-6; 3-hexanol, 623-37-0; 3-ethyl-3-pentanol, 597-49-9; phenol, 108-95-2; *n*-hexylamine, 111-26-2; 1-hexanethiol, 111-31-9; benzenethiol, 108-98-5; caproaldehyde, 66-25-1; benzaldehyde, 100-52-7; 2-heptanone, 110-43-0; 2-heptanol, 543-49-7; norcamphor, 497-38-1; norborneol, 1632-68-4; acetophenone, 98-86-2; α-phenylethanol, 98-85-1; benzophenone, 119-61-9; benzhydrol, 91-01-0; cinnamaldehyde, 104-55-2; cinnamyl alcohol, 104-54-1; 3-phenyl-1-propanol, 122-97-4; 2-methylcyclohexanone, 583-60-8; *cis*-2-methylcyclohexanol, 7443-70-1; 3-methylcyclohexanone, 591-24-2; 3-methylcyclohexanol, 591-23-1; 4-methylcyclohexanone, 589-92-4; 4-methylcyclohexanol, 589-91-3; 4-*tert*-butylcyclohexanone, 98-53-3; 4-*tert*-butylcyclohexanol, 98-52-2; 3,3,5-trimethylcyclohexanone, 873-94-9; 3,3,5-trimethylcyclohexanol, 116-02-9; *p*-benzoquinone, 106-51-4; hydroquinone, 123-31-9; anthraquinone, 84-65-1; 9,10-dihydro-9,10-anthracenediol, 58343-58-1; caproic acid, 142-62-1; benzoic acid, 65-85-0; acetic anhydride, 108-24-7; succinic anhydride, 108-30-5; phthalic anhydride, 85-44-9; caproyl chloride, 142-61-0; benzoyl chloride, 98-88-4; ethyl caproate, 123-66-0; ethyl benzoate, 93-89-0; phenyl acetate, 122-79-2; γ-butyrolactone, 96-48-0; phthalide, 87-41-2; isopropenyl acetate, 108-22-5; 1,2-butylene oxide, 106-88-7; styrene oxide, 96-09-3; cyclohexene oxide, 286-20-4; 1-methyl-1,2-cyclohexene oxide, 1713-33-3; caproamide, 628-02-4; benzamide, 55-21-0; *N,N*-dimethylbutyramide, 760-79-2; *N,N*-dimethylbenzamide, 611-74-5; capronitrile, 628-73-9; benzonitrile, 100-47-0; 1-nitropropane, 108-03-2; nitrobenzene, 98-95-3; azoxybenzene, 495-48-7; azobenzene, 103-33-3; cyclohexanone oxime, 100-64-1; phenyl isocyanate, 103-71-9; pyridine, 110-86-1; pyridine *N*-oxide, 694-59-7; di-*n*-butyl disulfide, 629-45-8; *n*-butyl mercaptan, 109-79-5; diphenyl disulfide, 882-33-7; dimethyl sulfoxide, 67-68-5; diphenyl sulfone, 127-63-9; methanesulfonic acid, 75-75-2; *p*-toluenesulfonic acid, 104-15-4; cyclohexyl tosylate, 953-91-3; *tert*-hexyl-*n*-octylchloroborane, 75052-81-2; dicyclopentylchloroborane, 36140-18-8; di-*n*-pentylchloroborane, 18379-77-6; 1-decene, 872-05-9; 1-decanol, 112-30-1; 6-chloro-1-hexene, 928-89-2; 6-chlorohexanol, 2009-83-8; 1-octene, 111-66-0; 1-octanol, 111-87-5.

(16) Brown, H. C.; Negishi, E. *J. Am. Chem. Soc.* **1967**, *89*, 5285. Manuscript in preparation: Brown, H. C.; Nazer, B.; Sikorski, J. A.

Organoboranes. 35. Reaction of Alkylthioboronic Esters with Trichloromethyllithium: Preparation of One-Carbon-Extended Carboxylic Acids and Thioacetals from Alkenes via Hydroboration

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Received September 12, 1983

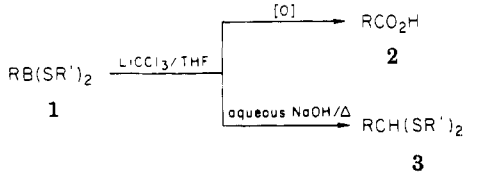
Various 2-alkyl-1,3,2-dithiaborolanes, $RB(S_2C_2H_4)$ (**1**), were converted to the corresponding carboxylic acids, RCO_2H (**2**), by using $LiCCl_3$ in THF, followed by oxidation with alkaline hydrogen peroxide. For R = hexyl, a reaction intermediate is converted by solvent into another compound, $C_6H_{13}C(S_2C_2H_4)B[O(CH_2)_4Cl]_2$ (**9a**), characterized spectroscopically. The yields of **2** decreased with increasing bulkiness of the alkyl groups R. Although the configuration of R = *trans*-2-methylcyclopent-1-yl (**1k**) was retained in the product (>98% trans), a significant degree of epimerization took place for R = *exo*-norbornyl (**1j**) during the oxidation (exo:endo = 86:14). More uniquely, the intermediates **9** were easily hydrolyzed by heating the reaction mixture with aqueous NaOH to give the corresponding 2-alkyl-1,3-dithiolanes **3**. Stereochemical integrity was retained in the products derived from **1j** and **1k**. Since **1** was prepared by the hydroboration of alkenes, this sequence provides a new method for introducing oxycarbonyl or thioacetal functionality into alkenes in a regioselective manner, and, in the case of **3**, also with stereocontrol.

Organylboronic esters, $RB(OR')_2$, bearing only one organyl group, would have a major advantage over triorganylboranes, R_3B, in organic synthesis when a single organyl group is to be incorporated into the product.

Recently, a few α-heteroatom-substituted carbanions have been found effective for homologating boronic esters. Thus, as reported by Matteson and co-workers, dichloromethyllithium converts $RB(OR')_2$ to $RCHClB(OR')_2$[1] and

0022-3263/84/1949-0892$01.50/0

Scheme I



chloro(trimethylsilyl)methyllithium provides RCH(SiMe$_3$)B(OR′)$_2$.[2] We found that methoxy(phenylthio)methyllithium was also effective for homologating RB(OR′)$_2$. With the aid of $Hg^{II}Cl_2$ to facilitate the transfer stage, it gives RCH(OMe)B(OR′)$_2$, which can be cleanly oxidized to aldehydes, RCHO.[3]

Except for these carbanionic reagents, however, many reagents failed to react with boronic esters. For example, dichloro(methoxy)methyllithium generated in situ from α,α-dichloromethyl methyl ether and lithium 1,1-diethylpropoxide converts R_3B to R_3COH[4] and R_2BOR' to $R_2C{=}O$,[5] while RB(OR′)$_2$ is unreactive to this reagent, giving practically none of the desired RCO_2H. Our efforts to synthesize carboxylic acids with the same class of reagents were all unsuccessful.[6]

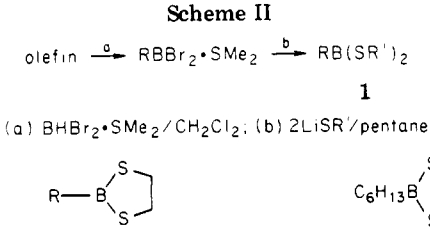
In connection with this problem, it should also be noted that some analogous reagents have been applied to R_3B in an attempt to control and limit the number of the alkyl groups being transferred. Although 2-chloro-2-lithiobenzo-1,3-dioxole,[7] 4,4-dimethyl-2-lithio-2-oxazoline,[8] and tris(phenylthio)methyllithium[9] have been found unique in their ability to limit alkyl group transfer to the second stage, giving ketones after oxidation, none of them has succeeded in stopping the transfer at the first stage.

These problems associated with RB(OR′)$_2$ as well as R_3B might be solved by utilizing monoorganylboranes bearing heteroatoms other than oxygen. We considered the alkylthioboronic esters RB(SR′)$_2$ (1), promising since they are stronger Lewis acids[10] and thus exhibit a higher reactivity to these nucleophilic reagents. Furthermore, ^{11}B NMR chemical shift values[11] of 1 (δ 60–88) are much closer to those of R_3B (δ 80–85) than those of RB(OR′)$_2$ (δ 30–35), and therefore, the similarity between 1 and R_3B might occur in their reactions also.

Since sulfur-substituted organoboranes had not been studied extensively,[12] we tested such representative reagents as carbon monoxide, ethyl diazoacetate, and trichloromethyllithium, all of which work with R_3B[12] but not with RB(OR′)$_2$.[13]

Although the first two reagents were inert to 1,[14] $LiCCl_3$ was reactive. Subsequent oxidation of the reaction in-

Scheme II



1a, R = hexyl
1e, R = 2-methylpentyl
1f, R = 3-methylbutyl
1g, R = 3,3-dimethylbutyl
1h, R = 2-(3-cyclohexen-1-yl)ethyl
1i, R = cyclohexyl
1j, R = *exo*-norbornyl
1k, R = *trans*-2-methylcyclopent-1-yl
1l, R = 1-ethylbutyl
1m, R = 1,1,2-trimethylpropyl

1b

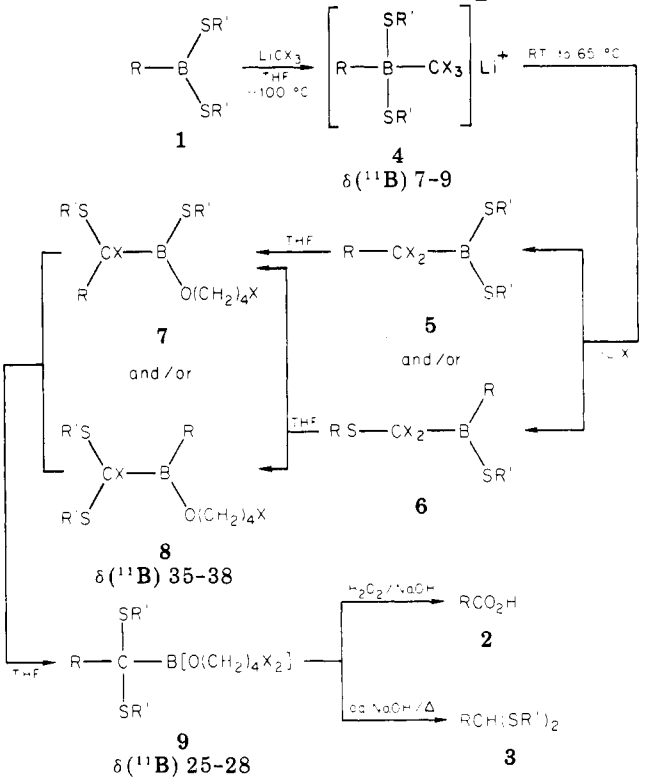
$C_6H_{13}B(SMe)_2$

1c

$C_6H_{13}B(SPh)_2$

1d

Scheme III



(1) (a) Matteson, D. S.; Majumdar, D. *J. Am. Chem. Soc.* **1980**, *102*, 7588. (b) Matteson, D. S.; Ray, R. *Ibid.* **1980**, *102*, 7590. (c) Matteson, D. S.; Sadhu, K. M. *Ibid.* **1983**, *105*, 2077.

(2) (a) Matteson, D. S.; Majumdar, D. *J. Organomet. Chem.* **1980**, *184*, C41; (b) *Organometallics* **1983**, *2*, 230.

(3) Brown, H. C.; Imai, T. *J. Am. Chem. Soc.* **1983**, *105*, 6285.

(4) (a) Brown, H. C.; Carlson, B. A.; Prager, R. H. *J. Am. Chem. Soc.* **1971**, *93*, 2070. (b) Brown, H. C.; Carlson, B. A. *J. Org. Chem.* **1973**, *38*, 2422. (c) Brown, H. C.; Katz, J.-J.; Carlson, B. A. *Ibid.* **1973**, *38*, 3968.

(5) Carlson, B. A.; Brown, H. C. *J. Am. Chem. Soc.* **1973**, *95*, 6876.

(6) As briefly mentioned previously (ref 3), by testing such carbenoid reagents as $CHCl_2OMe$ ($CHCl_3$, $CHCl_2F$, or $CHClF_2$)/$LiOCEt_3$/THF/0 °C, $CHBr_3$/LiTMP/THF/−78 °C, and $LiCCl_3$/THF/−100 °C with several typical esters of hexylboronic acid (trimethylene, dimethylene, tetramethyldimethylene, *O*-phenylene, methyl, and isopropyl esters), only 0–17% (in most cases <6%) yield of haptanoic acid was detected by GC in the oxidation products.

(7) Hara, S.; Kishimura, K.; Suzuki, A. *Tetrahedron Lett* **1978**, 2891.

(8) Baba, T.; Suzuki, A. *Synth. Commun.* **1983**, *13*, 367.

(9) Pelter, A.; Rao, J. M. *J. Chem. Soc., Chem. Commun.* **1981**, 1149.

(10) Egan, B. Z.; Shore, S. G.; Bonnell, J. E. *Inorg. Chem.* **1964**, *3*, 1024.

(11) Nöth, H.; Wrackmeyer, B. "NMR Basic Principles and Progress"; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1978; Vol. 14.

(12) (a) Negishi, E. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1983; Vol. 7, Chapter 45.6–45.11. (b) Pelter, A.; Smith, K. In "Comprehensive Organic Chemistry", Barton, D. H. R., Ollis, W. D., Jones, D. N., Eds.; Pergamon Press: Oxford, England, 1979; Vol. 3, Part 14. (c) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

(13) Brown, H. C.; Imai, T., unpublished results.

(14) Practically no reaction was observed between **1a** and CO, even under drastic conditions such as heating a dichloromethane solution in a bomb at 150 °C under 1500 psi pressure of CO (brown, H. C.; Nazer, B.; Cha, J. S.; Imai, T., unpublished results). Although ethyl diazoacetate reached with **1a** in refluxing THF to give ethyl heptanoate, the reaction was so slow that the reaction is not practical (5% yield after 18 h) and a large amount of starting materials remained unchanged (Brown, H. C.; Imai, T., unpublished results).

termediates gave carboxylic acids **2**. More uniquely, basic hydrolysis instead of oxidation produced thioacetals **3** of the corresponding aldehydes (Scheme I). This paper described procedures for these two transformations and considers some mechanistic aspects.

Starting Alkylthioboronic Esters 1. Five-membered cyclic esters of alkylthioboronic acids have been prepared directly by hydroboration of alkenes with 1,3,2-dithiaborolane.[15] Alternatively and more generally, **1** can be prepared from alkyldihaloboranes by treating with the metal salt of an appropriate thiol.[16]

In the present study, the latter method was adopted because of the ready availability of alkyldihaloboranes or their methyl sulfide adducts via the application of dihaloborane hydroborating agents[17] and their considerable flexibility for conversion into a variety of thioester functionalities. Thus, alkenes were hydroborated with $BHBr_2{\cdot}SMe_2$,[17b] and the resulting alkyldibromoborane–methyl sulfide adducts, with or without isolation, were cleanly converted to **1** by treatment with a suspension of lithium alkylthiolate in pentane (Scheme II).

The products were isolated by vacuum distillation in high yields (86–97%) and in high purity (by GC and/or NMR). All of the esters **1** had a singlet peak on ^{11}B NMR in a range of δ 67–75, reasonable for this class of compounds.[11]

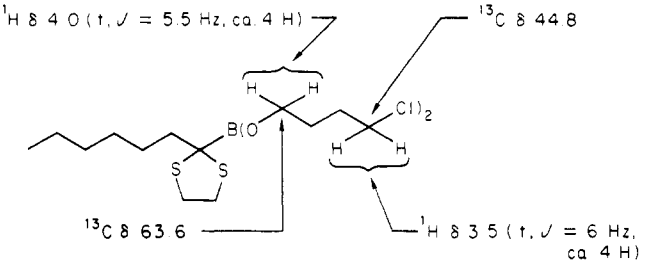
Preparation of Carboxylic Acids 2. In preliminary experiments, four selected esters of hexylthioboronic acid **1a–d** were prepared and reacted with two carbanionic reagents, $LiCCl_3$, pre-formed at −110 to −100 °C from $CHCl_3$ and *n*-BuLi[18] and $LiCBr_3$, generated in situ at −78 °C from $CHBr_3$ and lithium tetramethylpiperidide (LiTMP),[19] both in THF. Spectroscopic observation of the reaction mixture of the thioboronates and $LiCCl_3$ showed the existence of the ate complex, intermediate **4**, at δ 7–9 (Scheme III). This gradually decreased at room temperature and completely disappeared after 1 h of gentle reflux, while the ate complex produced by $LiCBr_3$ disappeared within 2 h at room temperature. In either case, as the ate complex peak disappeared, an increase in a second peak at δ 35–38 was observed. Then this peak decreased with concurrent formation of a third peak at δ 25–28. The absolute and relative rates of these changes were different for each compound.

Neither of these two peaks can, however, be attributed to a simple alkyl-migration nor a sulfur-migration product, **5** or **6**, respectively.[20] These species are expected to appear in a range of δ 60–75.[11] The observed chemical shift values suggested formation of an oxygen-bound boron species, most likely by incorporating the solvent THF. In a reaction of **1a** and $LiCCl_3$, after 1 h of reflux, the ate complex peak (δ 8) and the second peak (δ 35) had disappeared to give a single peak at δ 28. Solvent evaporation and spectroscopic observation of the product indeed indicated the formation of **9a** as the major component. In Scheme III, the second intermediate peak was tentatively assigned to **7** and/or **8**.

Table I. Preparation of One-Carbon-Extended Carboxylic Acids (2) from 2-Alkyl-1,3,2-dithiaborolanes (1) by Reaction with Trichloromethyllithium Followed by Alkaline Hydrogen Peroxide Oxidation[a]

	RCO_2H	yield,[b] %
1a	heptanoic acid (**2a**)	86 (91)[c]
1e	3-methylhexanoic acid (**2e**)	73
1f	4-methylpentanoic acid (**2f**)	74 (80)
1g	4,4-dimethylpentanoic acid (**2g**)	73
1h	3-(3-cyclohexen-1-yl)propanoic acid (**2h**)	58
1i	cyclohexanecarboxylic acid (**2i**)	67 (70)[c]
1j	*exo*-norbornanecarboxylic acid (**2j**)[d]	62 (75)
1k	*trans*-2-methylcyclopentanecarboxylic acid (**2k**)[e]	44 (47)
1l	2-ethylpentanoic acid (**2l**)	(19)
1m	(2,2,3-trimethylbutanoic acid (**2m**))	(≤1)[c]

[a] All reactions were done on a 5-mmol scale, and the oxidation was done by adding 6 N NaOH (15 mmol) and 10 M H_2O_2 (25 mmol) at <40 °C and stirring at room temperature for 3 h, unless otherwise indicated. [b] Isolated and/or GC yield, the latter given in parentheses. [c] The oxidation was done by adding 6 N NaOH (25 mmol) and 10 M H_2O_2 (25 mmol) at <50 °C and stirring at 60 °C for 2 h. [d] Contaminated by ca. 14% of the endo isomer (by ^{13}C NMR). [e] Almost pure trans (>98% by ^{13}C NMR).



In the early stages of the reaction with **1a**, a small transient peak attributable to **5** and/or **6** was observed at δ 66. Their reaction with the solvent seems to be unexpectedly faster than other steps.

Conversion of the intermediate **7** and/or **8** into **9** seems not to be in agreement with the earlier observation by Matteson: LiCHClSPh did not homologate alkylboronic esters.[2a] The difference is, however, that **7** and **8** are neutral species while Matteson's intermediate, if formed, would be an anionic ate complex, which would dissociate into reactants. Either in **7** or **8**, the C–X bond would easily dissociate heterolytically because of the existence of the alkylthio substituent(s) on the same carbon. Importance of such S_N1 character in the transition state (Wagner–Meerwein type) has been discussed previously.[3]

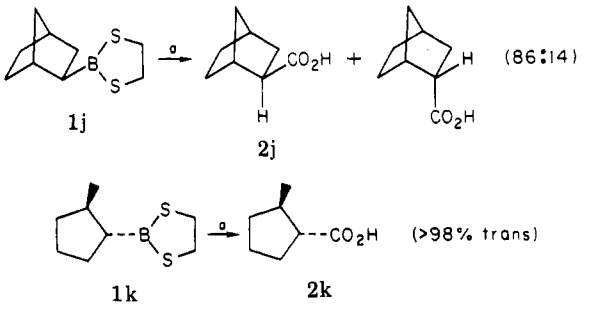
The intermediate **9** was oxidized by adding 6 *N* NaOH (5 molar equiv) and 10 *M* H_2O_2 (5 molar equiv) while maintaining the temperature below 50 °C and then heating the mixture to 60 °C for 2 h to afford heptanoic acid. The yields of the acid were as follows (thioboronate, % yield with $LiCCl_3$, % yield with $LiCBr_3$): **1a**, 91, 75; 1b, 49, 58; 1c, 54, 16 and 1d, 65, not examined.

Since good results were obtained with **1a** and $LiCCl_3$, 2-alkyl-1,3,2-dithiaborolanes of various alkyl structures **1e–m** were then prepared and examined with this reagent (Table I).

We also found that the oxidation was quite sensitive to the bulkiness of the organyl groups and to the reaction conditions. The result with the tertiary alkyl derivative

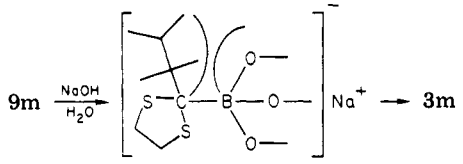
(15) Thaislivongs, S.; West, J. D. *J. Org. Chem.* **1977**, *42*, 3243.
(16) Cragg, R. H.; Lappert, M. F. *Organomet. Chem. Rev.* **1966**, *1*, 43.
(17) (a) Brown, H. C.; Ravindran, N. *Inorg. Chem.* **1977**, *16*, 2938. (b) Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1980**, *45*, 384. (c) Brown, H. C.; Campbell, J. B., Jr. *Ibid.* **1980**, *45*, 389.
(18) Köbrich, G.; Flory, K.; Drischel, W. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 513.
(19) Taguchi, H.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 3010.
(20) There is a precedent for exclusive sulfur migration in competition with a methyl group: The reaction of $CH_2ClB(CH_3)_2$ and CH_3SH gives $CH_3SCH_2B(CH_3)_2$ (Rathke, J.; Schaeffer, R. *Inorg. Chem.* **1972**, *11*, 1150). However, the methyl group is known to have significantly lower migratory aptitude compared with higher alkyl groups in a related 1,2-migration reaction (Zweifel, G.; Fisher, R. P. *Synthesis* **1974**, 339–340).

Scheme IV[a]



[a] (a) $LiCCl_3$/THF/−100 °C; (ii) NaOH/H_2O_2.

1m was exemplary since it gave thioacetal 2-(1,1,2-trimethylpropyl)-1,3,2-dithiolane **3m** exclusively (72% yield by GC) instead of the expected 2,2,3-trimethylbutanoic acid **2m** under the same oxidative workup. The thioacetal **3m** might have formed by basic hydrolysis of the intermediate **9m** and, the B–C bond cleavage would have been



facilitated by the steric repulsion between the bulky alkyl group and the boron substituents. A similar problem for such a competitive hydrolysis of the B–C bond in the alkaline hydrogen peroxide oxidation has been reported for the 1-(phenylthio)alkylboron compounds.[21]

Oxidation conditions were then reinvestigated with the norbornyl derivative **1j**, and optimum conditions (3 molar equiv of NaOH and 5 molar equiv of H_2O_2/≤40 °C and then room temperature/3 h)[22] were adopted for subsequent reactions. All reactions were done in 5-mmol scale, and the yields of **2** were estimated by GC with tetradecane as the internal standard. The carboxylic acids **2** were then isolated by extraction into 0.5 *N* NaOH, acidification with 3 *N* HCl, reextraction with ether, and bulb-to-bulb distillation.

Although the yield of **2** dropped markedly for the acyclic secondary alkyl derivative **1l**, primary and cyclic secondary alkyl derivatives gave good to fair yields of the corresponding carboxylic acids. For primary alkyl derivatives, 2- or 3-methyl- and 3,3-dimethyl branching is tolerated (see 1e–g).

The configuration of **1k** attained by hydroboration of 1-methylcyclopentene was retained in the product **2k**, the ^1H NMR spectrum of which agreed with that reported for the trans isomer.[23] Its ^{13}C NMR spectrum, however, showed a set of minor peaks (1–2%), which may be attributable to the cis isomer. On the other hand, the *exo*-norbornyl derivative **2j** obtained from **1j** (>98% exo) was contaminated by a considerable amount of the endo isomer (exo:endo ~ 86:14 based on ^{13}C NMR[24]). Since the migration proceeds with retention of configuration at the migrating carbon (vide infra), epimerization during the oxidation in a basic medium must be responsible for the stereochemical outcome (Scheme IV).

Table II. Preparation of 2-Alkyl-1,3-dithiolanes (3) from 2-Alkyl-1,3,2-dithiaborolanes (1) by Reaction with Trichloromethyllithium Followed by Alkaline Hydrolysis[a]

		 yield,[b] %
1a	2-hexyl-1,3-dithiolane (3a)	(67)
1e	2-(2-methylpentyl)-1,3-dithiolane (3e)	61 (64)
1i	2-cyclohexyl-1,3-dithiolane (3i)	(76)
1j	2-(*exo*-norbornyl)-1,3-dithiolane (3j)	71 (83)
1k	2-(*trans*-2-methylcyclopent-1-yl)-1,3-dithiolane (3k)	85, 90[c] (91)
1l	2-(1-ethylbutyl)-1,3-dithiolane (3l)	(82)
1m	2-(1,1,2-trimethylpropyl)-1,3-dithiolane (3m)	(81)

[a] The reactions were done on a 5-mmol scale, unless otherwise indicated. [b] Isolated and/or GC yield, the latter given in parentheses. [c] The reaction was done on a 11-mmol scale.

Preparation of Thioacetals 3. The formation of **3m** from **1m** in the reaction described above led us to investigate the hydrolytic cleavage of the **B–C** bond of the intermediate **9**, instead of the oxidative cleavage. Indeed, when the reaction mixture of **1** and $LiCCl_3$ was simply heated with aqueous NaOH, the corresponding thioacetals **3** were generally obtained (Scheme III).

The basic hydrolysis of **9** and isolation of **3** could be conveniently achieved by adding 6 *N* NaOH (3 molar equiv) and steam distilling the product. By this procedure, **1a** gave 67% GC yield of 2-hexyl-1,3-dithiolane (**3a**), which was isolated by GC. The product was identical with an authentic sample prepared by the thioacetalization of heptanal with 1,2-ethanedithiol.

Alkaline conditions are essential since steam distillation without addition of alkali resulted in only 2% of the product. The amount of NaOH may be reduced to 2.2 molar equiv, if desirable, to give 64% yield of **3a**, while use of excess NaOH (5 molar equiv) gave no improvement (56% yield of **3a**). Two moles of NaOH might be neutralized by replacing the alkoxy groups of **9** to regenerate THF molecules,[25] and the hydrolysis itself will proceed catalytically. When the steam distillation is undesirable, the solvolytic cleavage can be achieved also by heating the reaction mixture with MeONa/MeOH or EtONa/EtOH (3 *M*, 3 molar equiv in both cases) under gentle reflux for 3 h. Under these conditions, **1a** gave **3a** in 66% and 69% yield, respectively.

The steam distillation with 3 molar equiv of NaOH was adopted as the standard procedure, and the other esters of hexylthioboronic acid **1b–d** were tested. The six-membered cyclic ester **1b** also gave a moderate yield (53% by GC) of 2-hexyl-1,3-dithiane (**3b**), while the acyclic ester **1c** gave a mixture of several products, which were not examined further. For reaction with **1d**, the hydrolysis was done by adding 3 molar equiv of 6 *N* NaOH and heating the mixture under reflux for 1.5 h because the product **3d** could not be steam distilled effectively. By extraction with ether and distillation, **3d** was isolated in 34% yield.

Some 2-alkyl-1,3,2-dithiaborolanes **1e and 1i–m** were then examined by the standard procedure (Table II). In most cases, the products were isolated by preparative GC after their yields were estimated. Some of them were

(21) Yamamoto, S.; Shiono, M.; Mukaiyama, T. *Chem. Lett.* **1973**, 961.

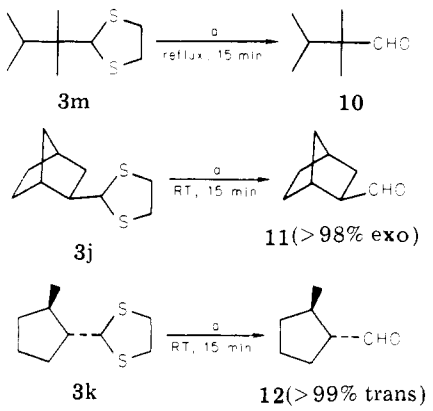
(22) Longer reaction times (12 h), larger excess of H_2O_2 (10 molar equiv), and inverse addition of the reaction mixture to the oxidant (3 molar equiv of NaOH/5 molar equiv of H_2O_2) gave comparable results, while a lesser amount of H_2O_2 (3 molar equiv) resulted in only 18% yield of the acid. Attempted oxidation in a phosphate buffer (pH 8) was unsuccessful, giving only 14% yield of the product. Competitive oxidation of sulfur may be a problem, particularly in the less basic medium (Brown, H. C.; Mandel, A. K. *J Org. Chem.* **1980**, *45*, 916).

(23) (a) Meyers, A. I.; Mihelich, E. D.; Kamata, K. *J. Chem. Soc., Chem. Commun.* **1974**, 768. (b) Pelter, A.; Hutchings, M. G.; Smith, K.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 1* **1975**, 145.

(24) Brouwer, H.; Stothers, J. B.; Tan, C. T. *Org. Magn. Reson.* **1977**, *9*, 361.

(25) Although quantitative analysis was not performed, the steam distillate obtained without addition of alkali was acidic on pH paper test.

Scheme V[a]



[a] (a) red $HgO/BF_3 \cdot OEt_2/H_2O$/THF.

isolated by distillation from independent runs. Although a crude product obtained by the steam distillation was generally contaminated by a minor amount of some polar impurity, it could be easily removed by a short alumina column, eluting with a pentane–ether mixture. Solvent evaporation and distillation gave pure dithiolanes.

Interestingly, **1** with relatively bulky alkyl groups gave higher yields of **3**. This may, at least partially, be due to the steric effect discussed earlier. On the contrary, the afore-mentioned aldehyde synthesis from alkylboronic esters[3] proceeds smoothly with primary and secondary alkyl derivatives but failed with a tertiary alkyl compound. The present reaction thus complements the aldehyde synthesis. Actually, **3m** could be cleanly hydrolyzed to 2,2,3-trimethylbutanal (**10**) by the method of Vedejs and Fuchs,[26] although brief heating was required (Scheme V).

The position α to the thioacetal moiety is not susceptible to epimerization, and thus **3j** was obtained in high isomeric purity (>98% by ^{13}C NMR). It was hydrolyzed by the same method as above to the corresponding aldehyde **11**, the ^{13}C NMR spectrum of which was identical with that of the exo isomer previously prepared by the afore-mentioned aldehyde synthesis.[3] Although **3k** was contaminated by a small amount of some impurity (1–2% by ^{13}C NMR), it might be the regioisomer of **3k**, 2-(1-methylcyclopent-1-yl)-1,3-dithiolane, since the hydroboration of 1-methylcyclopentene with $BHBr_2 \cdot SMe_2$ is known to produce 2% of 1-methylcyclopentylboron derivative as a minor regioisomer.[17b] Interestingly, however, this minor isomer could be removed by the dethioacetalization reaction to give the aldehyde **12** in almost pure form (≥99% by ^{13}C NMR). At room temperature, hydrolysis of the minor isomer might be significantly slower than that for **3k**, as observed for **3m** (see Experimental Section). Thus, at least for **3j** and **3k**, the epimerization was negligible under this dethioacetalization condition.

Conclusion

By taking advantage of the hydroboration reaction, this method provides the regioselective introduction of oxycarbonyl or thioacetal functionality into the less-substituted side of alkenes. The carboxylic acid synthesis is best achieved with terminal alkenes. On the other hand, the thioacetal synthesis works particularly well with 1,2-di-, tri-, and tetrasubstituted alkenes. In the thioacetal synthesis, the stereochemical integrity attained by hydroboration is retained in the products.

This study provides new scope for utilizing organothioboranes in organic synthesis and stimulates renewed interest for developing dithioborane hydroborating reagents that provide alkylthioboronic esters free from by-product.

(26) Vedejs, E.; Fuchs, P. L. *J. Org. Chem.* **1971**, *36*, 366.

Experimental Section

GC was performed with a Hewlett-Packard 5750 instrument. ^1H NMR spectra were obtained with a Varian T-60 spectrometer or, when indicated at 90 MHz, with a Perkin-Elmer R-32 spectrometer. ^{11}B NMR and wide-band ^1H-decoupled ^{13}C NMR spectra were obtained with a Varian FT-80A spectrometer. Chemical shift values are given in δ relative to Me_4Se in ^1H and ^{13}C NMR and relative to $BF_3 \cdot OEt_2$ in ^{11}B NMR. IR spectra were recorded with a Perkin-Elmer 137 spectrophotometer. Elemental analyses were done in the Purdue University Microanalytical Laboratory. Melting and boiling points are uncorrected.

THF was freshly distilled from benzophenone ketyl prior to use. Alkenes were distilled from LAH. Dibromoborane–methyl sulfide was prepared by the reported procedure[17a] and purified by distillation: bp 93–95 °C (0.15–0.1 torr) [lit.[27] bp 75 °C (0.1 torr)], colorless liquid that partially solidified on standing at room temperature.[28] The reagent was dissolved in dichloromethane and the concentration (4.75 *M*) was measured by hydride analysis.[12C] The following reagents were used without purification: 1,2-ethanedithiol (MCB), chloroform (J. T. Baker, photorex), bromoform (Aldrich). Several bottles of hexane solution of *n*-BuLi (Alfa) were estimated by Watson and Eastham's method as 2.16–2.34 *M* and used as such.

All reactions were done under nitrogen atmosphere by the same technique reported earlier.[3]

Preparation of Alkylthioboronic Esters 1. All of the thioboronic esters except **1m** were prepared from the corresponding alkyldibromoborane–methyl sulfide by treating with a suspension of lithium salt of an appropriate thiol in pentane on 50–200-mmol scale. The alkyldibromoborane–methyl sulfide adducts were prepared by hydroboration of olefins with $BHBr_2 \cdot SMe_2$ in dichloromethane and transferred directly into the flask in which a lithium alkylthiolate had been prepared, except for the hexyl-, 1-ethylbutyl-, and *trans*-2-methylcyclopentyl derivatives, which were isolated by distillation.[17b]

2-Hexyl-1,3,2-dithiaborolane (1a). General Procedure. In a 1-L flask equipped with a condenser and magnetic stirring bar were placed 1,2-ethanedithiol (200 mmol) and pentane (400 mL), and *n*-BuLi (400 mmol) was added slowly with rapid stirring and ice-water bath cooling. After 1 h of stirring at room temperature, neat hexyldibromoborane–methyl sulfide (200 mmol) was added dropwise, again with ice-water bath cooling. The stirring was continued for 2 h at room temperature. The flask was then attached to a simple distillation apparatus and flushed with nitrogen. The solvent was removed by distillation at atmospheric pressure, and the product was collected under vacuum (bath temperature, 150–180 °C (0.05 torr)). It was further purified by a second distillation with a Vigreux column: bp 65–69 °C (0.025 torr); 33.6 g (89%); ^{11}B NMR (CCl_4) δ 71 (s); ^1H NMR (CCl_4) δ 0.7–11 (m, 3 H), 1.1–1.7 (m, 10 H), 3.25 (s, 4 H).

2-Hexyl-1,3,2-dithiaborinane (1b) was obtained in 95% yield: bp 78–82 °C (0.025 torr); ^{11}B NMR (CCl_4) δ 63 (s); ^1H NMR (CCl_4) δ 0.6–1.6 (m, 13 H), 1.9–2.4 (m, 2 H), 2.7 (unresolved t, J = 5.0 Hz, 4 H).

Dimethyl hexyldithioboronate (1c) was obtained in 90% yield: bp 55–59 °C (0.04 torr); ^{11}B NMR (CCl_4) δ 67 (s); ^1H NMR (CCl_4) δ 0.6–1.1 (m, 3 H), 1.1–1.5 (m, 10 H), 2.2 (s, 6 H).

Diphenyl hexyldithioboronate (1d) was obtained in 94% yield: bp 118–121 °C (0.05 torr); ^{11}B NMR (CCl_4) δ 68 (s); ^1H NMR (CCl_4) δ 0.7–1.6 (m, 13 H), 7.1–7.5 (m, 10 H).

2-(2-Methylpentyl)-1,3,2-dithiaborolane (1e) was prepared from 2-methyl-1-pentene in 90% yield: bp 54–57 °C (0.03 torr); ^{11}B NMR (CCl_4) δ 70.4 (s); ^1H NMR (CCl_4) δ 0.7–11 [m containing d at 0.95 (J 6 Hz) 6 H], 1.1–1.7 (m, 7 H), 3.15 (s, 4 H).

(27) Kinberger, K.; Siebert, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1975**, *30B*, 55.

(28) This material, ^{11}B NMR (CH_2Cl_2) δ −7.5, was contaminated by a very small amount of $BBr_3 \cdot SMe_2$ (δ −10.5). Very pure material can be obtained by crystallization from dichloromethane (mp 30–33 °C: Campbell, J. B., Jr. Ph.D. Thesis, Purdue University, 1978).

2-(3-Methylbutyl)-1,3,2-dithiaborolane (1f) was prepared from 3-methyl-1-butene in 86% yield: bp 45–48 °C (0.03 torr); ^{11}B NMR (CCl_4) δ 71 (s); ^{1}H NMR (CCl_4) δ 0.95 (d, J 5 Hz, 6 H), 1.2–1.8 (m, 5 H), 3.2 (s, 4 H).

2-(3,3-Dimethylbutyl)-1,3,2-dithiaborolane (1g) was prepared from 3,3-dimethyl-1-butene in 85% yield: bp 57–61 °C (0.03 torr); ^{11}B NMR ($CDCl_3$) δ 71 (s); ^{1}H NMR ($CDCl_3$) δ 0.9 (s, 9 H), 1.3–1.6 (m, 4 H), 3.2 (s, 4 H).

2-[2-(3-Cyclohexen-1-yl)ethyl]-1,3,2-dithiaborolane (1h) was prepared from 3-vinylcyclohexene in 85% yield: bp 74–75 °C (0.03 torr); ^{11}B NMR ($CDCl_3$) δ 71 (s); ^{1}H NMR ($CDCl_3$) δ 0.8–2.3 (m, 11 H), 3.25 (s, 4 H), 5.4–5.95 (m, 2 H). The pattern of the olefinic proton region was characteristic of cyclohexene moiety and no peaks characteristic of the vinyl group was observed.

2-Cyclohexyl-1,3,2-dithiaborolane (1i) was prepared from cyclohexene (30% excess because of its low reactivity in the hydroboration reaction) in 94% yield (based on $BHBr_2{\cdot}SMe_2$): bp 65–67 °C (0.04 torr); ^{11}B NMR (CCl_4) δ 72 (s); ^{1}H NMR (CCl_4) δ 0.7–1.1 (m, 1 H), 1.1–2.1 (m, 10 H), 3.2 (s, 4 H).

2-(*exo*-Norbornyl)-1,3,2-dithiaborolane (1j) was prepared from norbornene (30% excess) in 97% yield (based on $BHBr_2{\cdot}SMe_2$): bp 80–83 °C (0.04 torr) [lit.[15] bp (bath temperature) 75 °C (0.7 torr)); ^{11}B NMR (CCl_4) δ 72 (s); ^{1}H NMR spectrum agreed with that reported.[15]

2-(*trans*-2-Methylcyclopent-1-yl)-1,3,2-dithiaborolane (1k) was prepared from (*trans*-2-methylcyclopentyl)dibromoborane–methyl sulfide in 92% yield: bp 59–62 °C (0.05 torr); ^{11}B NMR (CCl_4) δ 72 (s); ^{1}H NMR (CCl_4) δ 1.1 (d, J = 5 Hz, 3 H), 1.1–2.2 (m, 8 H), 3.2 (s, 4 H).

2-(1-Ethylbutyl)-1,3,2-dithiaborolane (1l) was prepared from (1-ethylbutyl)dibromoborane–methyl sulfide in 94% yield: bp 54–56 °C (0.03 torr); ^{11}B NMR (CCl_4) δ 72 (s); ^{1}H NMR (CCl_4) δ 0.7–11 (m, 6 H), 1.1–1.8 (m, 7 H), 3.2 (s, 4 H).

2-(1,1,2-Trimethylpropyl)-1,3,2-dithiaborolane (1m). (1,1,2-Trimethylpropyl)borane prepared from 2,3-dimethyl-2-butene (204 mmol) and neat $BH_3{\cdot}SMe_2$ (200 mmol) at 0 °C (ca. 2 h) was treated with 1,2-ethanedithiol (200 mmol). Initial hydrogen evolution was controlled by the rate of addition and occasional cooling with a cold-water bath. Stirring was continued overnight at room temperature to ensure thioboronate formation, and the product was distilled: bp 70–73 °C (0.06 torr); 36.7 g (96%); ^{11}B NMR (CCl_4) δ 74 (s); ^{1}H NMR (CCl_4) δ 0.85 (d, J = 6.5 Hz, 6 H), 1.0 (s, 6 H), 1.4–2.2 (m, 1 H), 3.2 (s, 4 H).

Preparation of Carboxylic Acids 2. All reactions were done on 5-mmol scale. The general procedure is given for the preparation of **2f**. Minor changes in the procedure, if any, are indicated individually. The yields are summarized in Table I. In all cases IR and ^{1}H NMR spectra of the products agreed with the proposed structure.

4-Methylpentanoic Acid (2f). A solution of $CHCl_3$ (5.5 mmol) in THF (10 mL) was prepared under nitrogen in a dry, 100-mL flask, which was equipped with a reflux condenser, septum-capped side arm, and a magnetic stirring bar, and was cooled with a cold ethanol bath maintained at *ca.* −100 °C by the occasional addition of liquid nitrogen. With stirring, *n*-BuLi (5.5 mmol) was added slowly through the cold surface of the reaction flask[29] over a period of 5 min. After 10 min of stirring at this temperature, **1f** (5.0 mmol) was added all at once by syringe, at which point, the slurry of $LiCCl_3$ immediately became a yellow solution, indicating very fast ate complex formation. The mixture was allowed to come to −20 °C in *ca.* 2 h. The cold bath was removed, and the stirring was continued for 2 h at room temperature and then for 1 h under gentle reflux. The oxidation was done by successive addition of 6 *N* NaOH (15 mmol) and 10 *M* H_2O_2 (25 mmol) while keeping the temperature below 40 °C with water-bath cooling. After being stirred for 3 h at room temperature, the mixture was acidified with 6 *N* HCl and saturated with salt. The product was extracted with ether (2 × 20 mL) and the extract dried over $MgSO_4$. Tetradecane was added as the internal standard, and the solution was analyzed by GC. The carboxylic acid was then extracted into aqueous NaOH (0.3 *N*, 2 × 15 mL) and re-extracted with ether (2 × 15 mL) after acidifying with 3 *N* HCl. The extract was dried over $MgSO_4$ and the solvent was removed by distillation. Vacuum distillation of the residue gave 0.43 g (74%) of **2f**: bp (bath temperature) 110–115 °C (13 torr); n^{20}_D 1.4142 [lit.[30] n^{20}D 1.4144].

Heptanoic Acid (2a). The oxidation was done by adding 6 *N* NaOH (25 mmol) and 10 *M* H_2O_2 (25 mmol) at temperatures below 50 °C and heating the mixture at 60 °C for 2 h. The general isolation procedure gave 0.56 g (86%) of **2a**: bp 84–85 °C (13 torr); n^{20}_D 1.4223 [lit.[31] n^{20}_D 1.4236]; IR and ^{1}H NMR spectra were identical with those of an authentic sample.

3-Methylhexanoic Acid (2e). By the general procedure, 0.48 g (73%) of **2e** was obtained: bp (bath temperature) 125–130 °C (13 torr); n_{20D} 1.4224 [lit.[32] n_{20D} 1.4227].

4,4-Dimethylpentanoic Acid (2g). By the general procedure, 0.47 g (73%) of **2g** was obtained: bp (bath temperature) 130–135 °C (13 torr) [lit.[33] bp 100–102 °C (15 torr)]; n^{20}_D 1.4195.

3-(3-Cyclohexen-1-yl)propanoic Acid (2h). By the general procedure, 0.45 g (58%) of **2h** was obtained: bp (bath temperature) 125–135 °C (0.05 torr). The distillate solidified on standing at room temperature: mp 32–35 °C [lit.[34] mp 33–35 °C]; ^{1}H NMR spectrum agreed with that reported.[35]

Cyclohexanecarboxylic Acid (2i). Oxidation was done by the same procedure given for **2a**. The general isolation procedure gave 0.43 g (67%) of **2i**: bp (bath temperature) 130–140 °C (13 torr); n^{20}_D 1.4568 [lit.[36] n^{20}_D 1.4599]; IR and ^{1}H NMR spectra were identical with those of an authentic sample.

***exo*-Norbornanecarboxylic Acid (2j).** Addition of **1j** to $LiCCl_3$ in THF was done dropwise slowly because the substrate tends to solidify at low temperature. Then the general procedure was followed, and 0.43 g (62%) of **2j** was obtained; bp (bath temperature) 150–155 °C (13 torr). Although the distillate solidified on standing at room temperature, it melted at considerably lower temperature (47–50 °C) than that reported [lit.[37] mp 58–58.5 °C]. ^{13}C NMR[24] showed that the product was contaminated by 14% of the endo isomer (as the average of peak height ratios). Shorter oxidation time did not improve the result (12% of the endo isomer).

***trans*-2-Methylcyclopentanecarboxylic Acid (2k).** By the general procedure, 0.28 g (44%) of **2k** was obtained: bp (bath temperature) 130–140 °C (13 torr); n^{20}_D 1.4456 [lit.[38] n^{20}_D 1.4521]; ^{1}H NMR agreed with that reported for the trans isomer;[23] ^{13}C NMR ($CDCl_3$) δ 19.7, 24.7, 30.1, 35.0, 39.5, 52.0, 183.2 (a set of minor peaks (<2% of the major peaks) were detected and may be attributable to the cis isomer).

2-Ethylpentanoic Acid (2l). By the general procedure, **2l** was prepared and isolated by preparative GC; n^{20}_D 1.4186 [lit.[39] n^{20}_D 1.4180].

Preparation of Aldehyde Thioacetals 3. All reactions were done on a 5-mmol scale, except for one reaction with **1k**. The general procedure is given for the preparation of **3k**, and minor modifications, if taken, are indicated individually. The yields of **3** are summarized in Table II.

2-(*trans*-2-Methylcyclopent-1-yl)-1,3-dithiolane (3k). The reaction of **1k** (5 mmol) and $LiCCl_3$ (derived from 10% excess reagents) was done by the same procedure described for the preparation of **2a**. After the reaction mixture had been refluxed for 1 h, the flask was attached to a steam distillation setup and 6 *N* NaOH (15 mmol) was added with rapid stirring. Steam was introduced slowly until most of the solvent had been distilled out and then vigorously while the flask was heated to 100–130 °C by an oil bath. The distillation was continued until the distillate became no longer turbid (usually 200–300 mL was collected). The aqueous phase was saturated with salt, and the product was

(29) This procedure (see ref 1a) gave a colorless or slightly yellow slurry of $LiCCl_3$ in THF.

(30) Hommelen, H. *Bull. Soc. Chim. Belg.* **1933**, *42*, 243.
(31) Vogel, A. I. *J. Chem. Soc.* **1948**, 1814.
(32) Quebedeaux, W. A.; Wash, G.; Ney, W. O.; Crouch, W. W.; Lochte, H. L. *J. Am. Chem. Soc.* **1943**, *65*, 767.
(33) Heilmann, R.; de Gaudemaris, G.; Heindl, R. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1954**, *239*, 1224.
(34) Marvell, E. N.; Knutson, R. S.; McEwen, T.; Sturmer, D.; Federici, W.; Salisbury, K. *J. Org. Chem.* **1970**, *35*, 391.
(35) Yurev, V. P.; Kuchin, A. V.; Tolstikov, G. A. *Izv. Akad. Nauk SSSR Ser. Khim. (Engl. Trans.)* **1974**, 817.
(36) Zelinsky, N. *Chem. Ber.* **1902**, *35*, 2687.
(37) Berson, J. A.; Ben-Efraim, D. A. *J. Am. Chem. Soc.* **1959**, *81*, 4083.
(38) Ney, W. O.; Crouch, W. W.; Rannefeld, C. E.; Lochte, H. L. *J. Am. Chem Soc.* **1943**, *65*, 770.
(39) Sy, M.; Bun-Hoi, N. P.; Dat-Xuong, N. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1954**, *239*, 1224.

extracted with ether (3 × 20 mL) and dried over $MgSO_4$. For the GC analysis, tetradecane was added as the internal standard. Isolation of the product was done by an independent run on the same scale and by the same procedure. The steam-distilled product was contaminated by a small amount of some polar material, probably a thiol, but not 1,2-ethanedithiol. The impurity was easily removed by a short alumina column (25 mm × 10 cm), eluting with pentane-ether mixture (95:5). Solvent evaporation and distillation gave pure **3k**: bp (bath temperature) 170–175 °C (14 torr); 0.80 g (85%); n^{20}_D 1.5475; IR (neat) 2900, 2850, 1460, 1430, 1380, 1280, 980, 860 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.9–1.4 [m containing d at 1.05 (J = 6.3 Hz), 4 H], 1.4–2.05 (m, 7 H), 3.0–3.35 (m, 4 H), 4.65 (d, J = 6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.7, 24.4, 31.3, 35.6, 38.7 (SCH_2), 38.8 (SCH_2), 40.4, 53.7, 58.8 (SCHS). A set of minor peaks (1.2% as the average of peak height ratios) were observed in the ^{13}C NMR spectrum. These peaks most likely are due to 2-(1-methylcyclopent-1-yl)-1,3-dithiolane rather than the cis isomer of **3k** (see the text). Anal. Calcd for $C_9H_{16}S_2$: C, 57.39; H, 8.56; S, 34.05. Found: C, 57.68; H, 8.75; S, 34.00.

The reaction was repeated on a 15-mmol scale, and the product was isolated in 90% yield; bp 136–139 °C (13 torr).

2-Hexyl-1,3-dithiolane (3a). By the general procedure, **3a** was prepared, estimated by GC, and then isolated by preparative GC; n^{20}_D 1.5181 [lit.[40] n^{20}_D 1.5189]. The product was identical with the authentic sample prepared from heptanal by the acid-catalyzed thioacetalization[41] with 1,2-ethanedithiol: bp 104–106 °C (0.3 torr) [lit.[40] bp 100.5–101 °C (1.1 torr)].

2-Hexyl-1,3-dithiane (3b).[42] By the general procedure, **3b** was prepared and isolated by GC: n^{20}_D 1.5197; ^1H NMR (CCl_4) δ 0.6–1.0 (m, 3 H), 1.0–1.8 (m, 10 H), 1.8–2.3 (m, 2 H), 2.5–2.9 (m, 4 H), 3.9 (t, J = 6 Hz, 1 H).

1,1-Bis(phenylthio)heptane (3d). Reaction of **1d** and $LiCCl_3$ was done by the general procedure. After the reaction mixture had been refluxed for 1 h, 6 N NaOH (15 mmol) was added, and the heating was continued for 1.5 h. The product was extracted with ether, purified by a silica gel column, eluting with pentane-dichloromethane mixture (90:10), and distilled: 0.54 g (34%), bp (bath temperature) 195–200 °C (0.04 torr) [lit.[43] bp (186–190 °C (2 torr)]; n^{20}_D 1.5820 [lit.[43] n^{20}_D 1.5869].

2-(2-Methylpentyl)-1,3-dithiolane (3e). By the general procedure, **3e** was prepared and isolated by GC: bp (bath temperature) 165–170 °C (13 torr); 0.59 g (61%); n^{20}_D 1.5171; IR (neat) 2950, 1480, 1440, 1390, 1280, 1170, 1115, 860 cm^{-1}; ^1H NMR (CCl_4) δ 0.7–1.1 (m, 6 H), 1.1–1.5 (m, 4 H), 1.5–1.9 (m, 3 H), 3.15 (AB t, J 5.5 Hz, 4 H), 4.4 (t, J 7 Hz, 1 H). Anal. Calcd for $C_9H_{18}S_2$: C, 56.78; H, 9.53, S, 33.69. Found: C, 56.86; H, 9.44; S, 33.79.

2-Cyclohexyl-1,3-dithiolane (3i).[44] By the general procedure, **3i** was prepared and isolated by GC: n^{20}_D 1.5583; IR (neat) 2900, 2840, 1460, 1430, 1280, 970, 905, 860 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.15 (m, 11 H), 3.15 (s, 4 H), 4.35 (d, J = 6.5 Hz, 1 H).

2-(*exo*-Norbornyl)-1,3-dithiolane (3j). Addition of **1j** to $LiCCl_3$ in THF was done dropwise slowly (see preparation of **2j**) and then the general procedure was followed. The product was isolated by distillation: bp (bath temperature) 115–125 °C (0.04 torr); 0.71 g (71%); n^{20}_D 1.5724; IR (neat) 2900, 2850, 1460, 1430, 1325, 1310, 1280, 1260, 1240, 1150, 930, 860 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.95–1.9 (m, 9 H), 2.1–2.3 (m, 2 H), 3.0–3.3 (m, 4 H), 4.25 (d, J = 10.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 28.7, 30.3, 35.6, 37.5, 37.9, 38.9 (2 × SCH_2), 42.5, 51.7, 60.2 (SCHS). Some small peaks (1–2% by peak height) were detected and may be due to the endo isomer. Anal. Calcd for $C_{10}H_{16}S_2$: C, 59.94; H, 8.05; S, 32.01. Found: C, 60.07; H, 7.99; S, 32.00.

2-(1-Ethylbutyl)-1,3-dithiolane (3l). By the general procedure, **3l** was prepared and isolated by GC: n^{20}_D 1.5227; IR (neat) 2910, 2860, 1475, 1430, 1385, 1280, 860 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.6–1.1 (m, 6 H), 1.1–1.9 (m, 7 H), 3.2 (AB t, J = 5.5 Hz, 4 H), 4.55–4.75 (m, 1 H). Anal. Calcd for $C_9H_{18}S_2$: C, 56.78; H, 9.53; S, 33.69. Found: C, 57.03; H, 9.54; S, 33.70.

2-(1,1,2-Trimethylpropyl)-1,3-dithiolane (3m). By the general procedure, **3m** was prepared and isolated by GC: n^{20}_D 1.5320; IR (neat) 2940, 1470, 1430, 1400, 1380, 1280, 1140, 860 cm^{-1}; ^1H NMR (CCl_4) δ 0.85 (d, J = ~6 Hz, 6 H), 0.9 (s overlapping with the left peak of the doublet, 6 H), 1.3–2.1 (m, 1 H), 3.1 (s, 4 H), 4.65 (s, 1 H). Anal. Calcd for $C_9H_{18}S_2$: C, 56.78; H, 9.53; S, 33.69. Found: C, 56.99; H, 9.76; S, 33.60.

Dethioacetalization. By the known procedure,[26] the following aldehydes were obtained from the corresponding thioacetals.

2,2,3-Trimethylbutanal (10). With red HgO (8 mmol) and BF_3·OEt_2 (8 mmol), **3m** (4 mmol) was hydrolyzed in 15% aqueous THF (8 mL). The reaction was complete in 15 min of reflux. Since the product was fairly volatile, it was difficult to obtain pure material by small-scale fractionation. The aldehyde was thus collected with the remaining THF under vacuum, bp 60–75 °C (110 torr), 0.48 g (65.4% of the total GC area comprised of **10**, roughly 69% yield) and was purified by GC isolation; n^{20}_D 1.4110. Since the melting point of its 2,4-dinitrophenylhydrazone (146–148 °C from EtOH) did not agree with that reported (158–159 °C[45]), **10** was characterized as follows: IR (neat) 2950, 2880, 2700, 1730 (CO), 1475, 1380, 1160, 1075, 910, 840 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.9 (d, J = 7 Hz, 6 H), 1.0 (s, 6 H), 1.65–2.15 (hept with fine splittings, 1 H), 9.45 (s, 1 H). Anal. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.53; H, 12.64. At room temperature hydrolysis was slow (59% conversion after 30 min), although the yield of **10** was high (91% based on conversion, both estimated by GC).

***exo*-Norbornanecarbaldehyde (11).** The hydrolysis of **3j** (3.2 mmol) had been completed after 15 min of stirring at room temperature. The product was isolated by distillation: bp (bath temperature) 80–85 °C (14 torr); 0.36 g (92%). Its ^{13}C NMR spectrum was identical with that of **11**, previously prepared by the boronic ester homologation,[3] and no appreciable amount of epimerization was detected.

***trans*-2-Methylcyclopentanecarbaldehyde (12).** By the same as above, **3k** (10 mmol) was hydrolyzed to the aldehyde: bp 86–88 °C (110 torr); 0.93 g (83%); n^{20}_D 1.4360. Its ^{13}C NMR spectrum was identical with that of **12** previously prepared.[3]

Acknowledgment. We gratefully acknowledge support from the National Science Foundation, Grant CHE 79-18881, for this research.

Registry No. **1a**, 88686-82-2; **1b**, 88686-96-8; **1c**, 88686-97-9; **1a**, 88703-11-1; **1e**, 88686-83-3; **1f**, 88686-84-4; **1g**, 88686-85-5; **1h**, 88686-86-6; **1i**, 88686-87-7; **1j**, 63076-48-2; **1k**, 88686-88-8; **1l**, 88686-89-9; **1m**, 88686-90-2; **2a**, 111-14-8; **2e**, 3780-58-3; **2f**, 646-07-1; **2g**, 1118-47-4; **2h**, 22482-62-8; **2i**, 98-89-5; **2j**, 934-29-2; **2k**, 4541-43-9; **2l**, 20225-24-5; **2m**, 49714-52-5; **3a**, 6008-84-0; **3e**, 88686-91-3; **3i**, 70777-60-5; **3j**, 88686-92-4; **3k**, 88686-93-5; **3l**, 88686-94-6; **3m**, 88686-95-7; **10**, 86290-37-1; **11**, 3574-55-8; **12**, 20106-44-9; *endo*-norbornanecarboxylic acid, 934-28-1; 1,2-ethanedithiol, 540-63-6; hexyldibromoborane–methyl sulfide, 64770-04-3; 1,3-propanedithiol, 109-80-8; methanethiol, 74-93-1; thiophenol, 108-98-5; 2-methyl-1-pentene, 763-29-1; 3-methyl-1-butene, 563-45-1; 3,3-dimethyl-1-butene, 558-37-2; 3-vinylcyclohexene, 766-03-0; cyclohexene, 110-83-8; norbornene, 498-66-8; (1-ethylbutyl)dibromoborane–methyl sulfide, 64770-06-5; (1,1,2-trimethylpropyl)borane, 3688-24-2; 2,3-dimethyl-2-butene, 563-79-1; (*trans*-2-methylcyclopentyl)dibromoborane–methyl sulfide, 72205-99-3.

(40) Newman, B. C.; Eliel, E. L. *J. Org. Chem.* **1970**, *35*, 3641.
(41) Jones, R. H.; Lukes, G. E.; Bashour, J. I. U.S. Pat. 2690988 (1954); *Chem. Abstr.* **1955**, *49*, P9868.
(42) No details are given in the literature (Ho, T.-L.; Ho, H. C.; Wong, C. M. *Can. J. Chem.* **1973**, *51*, 153. Vedejs, E.; Fuchs, P. L. *J. Org. Chem.* **1971**, *36*, 366.
(43) Vasileva, I.; Freidlina, R. Kh. *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1961**, 1049.
(44) No details are given in the literature (Olah, G. A.; Narang, S. C.; Salem, G. F.; Gupta, B. G. B. *Synthesis* **1979**, 273).
(45) Only the melting point of 2,4-DNP derivative is given: Hickinbottom, W. J.; Peters, D.; Wood, D. G. M. *J. Chem. Soc.* **1955**, 1360.