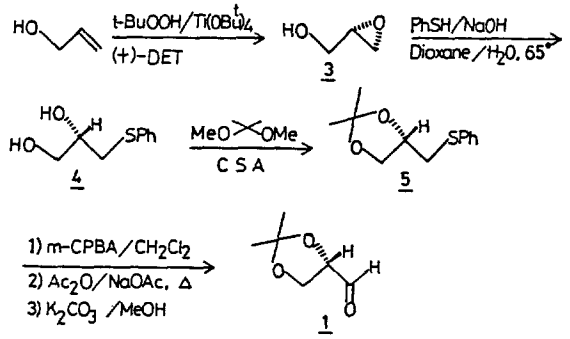

Scheme 1.

using 25% hexane-ether as eluents(Rf 0.26). The sulfoxide(**6**) was subjected to Pummerer rearrangement[9] (Ac_2O/NaOAc, reflux, 11h) and purified on TLC plate (eluted with 25% ether-hexane, Rf 0.37) to give the α-acetoxy sulfide(**7**)[8] in 81% yield. Treatment of α-acetoxy sulfide(**7**) with K_2CO_3/MeOH (reflux, 2h) afforded 2,2-dimethyl-1,3-dioxolane-4-carboxaldehyde, the (S)-enantiomer(**1**)[8]; bp45-47°C/15mmHg (lit.,[2] bp40.5-41.5°C/11mmHg); $[\alpha]_D^{20}$ -19.6°(c=0.34, MeOH). The compound synthesized was identical in all respects (TLC, IR, NMR, MS) with the compound reported in the literature.

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7. In the reference 6(a), Sharpless reported that allyl alcohol afforded 2(S)-glycidol, ca 15% yield, 73% ee performed at 0°C by using (+)-diisopropyl tartarate and $Ti(OiPr)_4$.
8. Satisfactory physical properties and spectroscopic data(^{1}H-NMR, IR, MS) were obtained for the compounds: diol(**4**); mp 61-64°C; TLC Rf 0.31(20% hexane-ether); IR(KBr, pellet) 3410, 3060, 1585, 1485cm^{-1}; ^{1}H-NMR(80 MHz, $CDCl^3$)δ 3.13(1H), 3.23(1H), 3.53(3H,m), 7.2-7.4(5H,m); MS 184(M^+), 109(Base). Phenylthio acetonide(**5**); IR(NaCl, neat) 3060, 1585, 1480cm^{-1}; ^{1}H-NMR δ 1.42 (3H,s) 1.43 (3H,s), 3.15 (2H,d), 3.73-4.45 (3H, m), 7.23-7.38 (5H,m). Sulfoxide(**6**); IR(NaCl, neat) 3060, 1585, 1050cm^{-1}; ^{1}H-NMR δ 1.42 (3H,s), 1.44 (3H,s), 2.95-3.10 (2H,d), 3.67-4.35 (3H,m), 7.23-7.38(5H,m). α-acetoxy sulfide(**7**); IR(NaCl, neat) 3060, 1735, 1585, 1190 cm^{-1}; ^{1}H-NMR δ 1.34(3H,s), 1.42(3H,s), 2.10(3H,s), 3.85-4.35(3H,m), 5.91-6.15(1H,d), 7.25-7.61(5H,m). (S)-enantiomer(**1**); IR(NaCl, neat) 2850, 2750, 1725 1180 cm^{-1}; ^{1}H-NMR δ 1.35 (3H,s), 1.46 (3H,s), 4.01-4.18 (2H,d), 4.24-4.39 (1H,m), 9.85 (1H,s).
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Selective Hydroboration of Alkenes and Alkynes with Thexyl-2-butoxyborane in the Presence of Ketones

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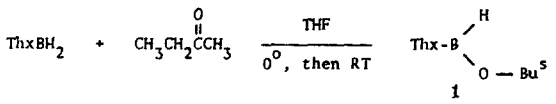
Various borane derivatives hydroborate alkenes and alkynes to produce organoboranes.[1] However these reagents also react fast with ketones.[2] Thus, in the presence of ketones, selective hydroborations of alkenes and alkynes, to our best knowledge, have never been achieved.

Recently, thexyl-2-butoxyborane, **1**, was prepared from the reaction of thexylborane ($ThxBH_2$) with an equimolar amount of 2-butanone (eq 1).



^{11}B nmr spectrum of **1** shows a doublet (J_{B-H}=146 Hz) at δ=50.6 ppm, whereas ^{11}B nmr chemical shift of $ThxBH_2$ is known to be 24.0 ppm.[3] The ir spectrum of $ThxBH_2$[4] shows the bridge-hydrogen band at 1565 cm^{-1} and the terminal boron-hydrogen band at 2640 cm^{-1}. However their spectrum of **1** in THF shows no bridge hydrogen band, but only the terminal boron-hydrogen band at 2413cm^{-1}. Apparently **1** exists as a monomeric species.

In the study of the reducing characteristics of **1** for representative functional groups, we have found that this new reagent reacted with aldehydes, terminal alkenes and alkynes

Table 1. Selective Hydroboration of Alkene and Alkyne with Thexyl-2-butoxyborane in the Presence of Ketone at 20°C

Entry	1:1 Mixture of compounds	Ratio of H^-/compd	Time h	Products, %[a] Hydroboration product	Reduction of ketone	Recovered ketone
1	1-Octene / 2-Heptanone	2.0[b]	12	87.5[e]	trace	100
2	1-Octene / 2-Heptanone	3.0[b]	12	98[e]	trace	100
3	1-Octene / Acetophenone	2.0[b]	12	84.5[e]	2	98
4	1-Octene / Acetophenone	3.0[c]	12	100[e]	2	98
5	Cyclohexene / 2-Heptanone	2.0[b]	12	67	18	82
6	Cyclohexene / 2-Heptanone	2.0[b]	24	86	21	79
7	Cyclohexene / 2-Heptanone	3.0[c]	12	100	24	76
8	Cyclohexene / Acetophenone	2.0[b]	12	65	15	85
9	Cyclohexene / Acetophenone	2.0[b]	24	90	21	79
10	Cyclohexene / Acetophenone	3.0[c]	12	96	20	80
11	1-Heptyne / Acetophenone	2.0	12	90[f]	3.5	96.5
12	Phenylacetylene / 2-Heptanone	2.0[b]	12	99[g]	trace	100
13	4,4-Dimethyl-6-heptyn-2-one	2.0[d]	12	76[h]	—	—

[a]Products were determined by glpc analyses after oxidative work-up. The concentrations were [b]0.4M, [c]0.7 M, and [d]1.2 M in compound. [e]The ration of 1-octanol/2-octanol was 95/5. [f]The oxidation was carried out by the addition of 30 % H_2O_2 solution, after the reaction mixture was adjusted to about pH 8 with 3N NaOH solution with the aid of phenol red indicator at room temperature, to give a 90% yield of heptanal. [g]The oxidation was carried out by the addition of 30% H_2O_2 solution in the presence of $Na_2B_4O_7$. [h]An isolated yield of 4,4-dimethyl-6-hepten-2-one.

rapidly but reduced ketones and other functional groups such as an ester, an amide and a nitrile very slowly. And alkynes were cleanly monohydroborated even in the presence of excess of **1**. This unique reducing characteristics of **1** encouraged us to explore its utility for the selective hydroboration of alkenes and alkynes in the presence of ketones.

The chemo-selectivity was tested for four alkene-ketone pairs, two alkyne-ketone pairs and an yn-one compound with 2 or 3 equivalents of **1** at room temperature. The reaction products were analyzed by glpc after oxidative work-up, or isolated by distillation after protonolysis.

As shown in Table 1, 1-octene could be selectively hydroborated in the presence of ketones in 12 h at room temperature using three equivalents of **1**. Thus the reaction of a 1:1 mixture of 1-octene and 2-heptanone with **1** yielded (after oxidative work-up) a 93% of 1-octanol and a 5% of 2-octanol and only a trace amount of 2-heptanol, leaving 2-heptanone intact. And the reaction of an equimolar mixture of 1-octene and acetophenone with **1** yielded (after oxidative work-up) a 95% of 1-octanol and a 5% of 2-octanol, leaving 98% acetophenone intact.

In the case of cyclohexene, the selectivity went down somewhat. Thus competitive reactions with a 1:1 mixture of cyclohexene and ketones such as 2-heptanone or acetophenone were only partially successful, about 20 % of ketones being attacked when the hydroboration of cyclohexene was completed.

On the other hand, the competitive reaction of a 1:1 mixture of 1-heptyne and acetophenone with two equivalents of **1** produced a 90 % yield of heptanal (after oxidation) and a 3.5% yield of 1-phenylethanol in 12 h. And phenylacetylene was selectively monohydroborated to give a 99 % yield of phenylacetaldehyde (after oxidation), with only a trace of 2-heptanone being reduced. Also, a 76 % yield of 4,4-dimethyl-6-hepten-2-one was isolated after protonolysis of the reaction product of 4,4-dimethyl-6-heptyn-2-one with two equivalents of **1** for 12 h at room temperature.

Thus, a new hydroborating agent, thexyl-2-butoxyborane, could be prepared conveniently by merely adding one molar equivalent of 2-butanone to $ThxBH_2$. And this reagent achieved a selective hydroboration of terminal alknenes and alkynes in the presence of ketones with an excellent selectivity. Other applications of this reagent in organic synthesis are under investigation.

The following is a typical experimental procedure. A reaction flask was charged with 0.23 m*l* of acetophenone (2 mmol), 0.29 m*l* of 1-octene (2 mmol) and 0.23 m*l* of dodecane (1 mmol) as an internal standard at room temperature. The reaction was started by the addition of 2.1 m*l* of 2.86 M **1**[5] (6 mmol) with stirring at room temperature. The resulting reaction mixture was 0.7 M in each compound and the ratio of hydride-to-compound was 3.0. After 12 h, 0.2 m*l* of glacial acetic acid was added dropwise at 0°.[6] After 5 minutes, the reaction mixture was neutralized with 5 N NaOH solution and made alkaline by adding 3 m*l* more of 5 N NaOH solution. The oxidation was carried out by the addition of 0.9 m*l* of 30% H_2O_2 solution at room temperature. After the oxidation was completed, aqueous layer was saturated with NaCl. The organic layer was separated and dried with anhydrous $MgSO_4$. The glpc analysis of the organic layer, showed a 95 % yield of 1-octanol, 5 % of 2-octanol, 98 % of acetophenone and a 2 % yield of 1-phenylethanol.

In the case of 4,4-dimethyl-6-heptyn-2-one, the product 4,4-dimethyl-6-hepten-2-one was isolated by distillation after protonolysis of the reaction product with glacial acetic acid. Identification of the product was made by nmr: δ0.97 (*s*,6,-CH_3), 2.0-2.23(*m*,7,$CH_3COCH_2CCH_2C=C$), 4.74-6.0 (*m*,3,-$CH=CH_2$) and the semicarbazone: mp 143°(lit.[7] 143°).

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6. When the hydrolysis of the reaction mixture was carried out by the addition of H_2O, ketone was reduced in the course of the hydrolysis. But AcOH destroyed the residual hydride immediately without allowing the further reduction of ketone. *c*-HCl–THF mixture was also satisfactory for the hydrolysis.
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