Reactions of Vinyloxyboranes with Carbonyl Compounds, Nitriles, and Formates[1)]

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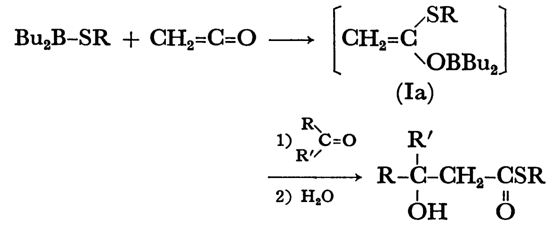
A new vinyloxyborane derivative, Id, was found to be formed in reaction of phenyl di-*n*-butylthioboronite (II) with methyl vinyl ketone. In order to explore its utilization in organic synthesis, the reactivity of Id and other known vinyloxyboranes was variously examined. Id and Ie gave *β*-hydroxyketones (IVa—c, Va—d) in fairly good yields when they were allowed to react with carbonyl compounds. The reaction of Ia′ and Ib with nitriles, followed by hydrolysis, afforded *β*-iminothioates (VIa—c) and *β*-ketoesters (VIIa—d) respectively. It was also found that the borane (Ib) reacted with formates or formamides at room temperature to give ethyl α-formylhexanoate.

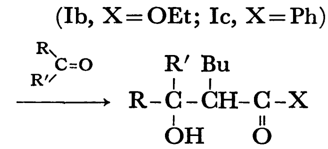
In a previous paper,[2)] it was reported that *β*-hydroxythioates are produced in high yields by the reaction[3)] of thioboronites, ketene, and carbonyl compounds *via* the key intermediates, vinyloxyboranes (Ia). Similarly,



$$\mathrm{Bu_2B\text{-}SR} + \mathrm{CH_2{=}C{=}O} \longrightarrow \left[\mathrm{CH_2{=}C}\begin{smallmatrix}\diagup \mathrm{SR}\\ \diagdown \mathrm{OBBu_2}\end{smallmatrix}\right] \xrightarrow[2)\ \mathrm{H_2O}]{1)\ \mathrm{RR'C{=}O}} \mathrm{R\text{-}\underset{OH}{\overset{R'}{C}}\text{-}CH_2\text{-}\underset{O}{\overset{}{\overset{\|}{C}}}SR}$$

(Ia)

vinyloxyboranes[4)] (Ib, Ic) prepared from tri-*n*-butylborane and ethyl diazoacetate or diazoacetophenone reacted with carbonyl compounds to afford *β*-hydroxyesters and *β*-hydroxyketones respectively.[1,3)]

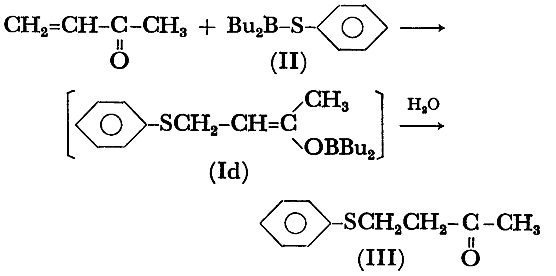


$$\mathrm{Bu_3B} + \mathrm{N_2CH\text{-}\underset{O}{\underset{\|}{C}}\text{-}X} \xrightarrow{-\mathrm{N_2}} \left[\mathrm{BuCH{=}C}\begin{smallmatrix}\diagup \mathrm{X}\\ \diagdown \mathrm{O\text{-}BBu_2}\end{smallmatrix}\right] \xrightarrow{\mathrm{RR'C{=}O}} \mathrm{R\text{-}\underset{OH}{\overset{R'}{C}}\text{-}\overset{Bu}{CH}\text{-}\underset{O}{\underset{\|}{C}}\text{-}X}$$

(Ib, X=OEt; Ic, X=Ph)

We have subsequently been studying the formation and reactivity of vinyloxyborane derivatives and now wish to report the formation of a new vinyloxyborane (Id), which was obtained from methyl vinyl ketone and thioboronite (II), and the reactivity of Id and Ie, which were prepared from tri-*n*-butylborane and methyl vinyl ketone,[5)] with various carbonyl compounds. This paper will also describe the reactions of Ia′ and Ib with such electophiles as nitriles, acyl halides, and formates.

A new vinyloxyborane (Id) was formed by the reaction of methyl vinyl ketone with thioboronite according to the following procedure: an equimolar amount of *S*-phenyl di-*n*-butylthioboronite (II) was added to a solution of methyl vinyl ketone in CCl_4, and then the mixture was kept standing at room temperature for 30 min. The product was not isolated, but its structure was confirmed to be (1-methyl-3-phenylthio-1-propenyloxy)di-*n*-butylborane (Id) by PMR analysis. This assignment was also supported by the observation that the hydrolysis of Id in aqueous methanol afforded 4-phenylthiobuta-2-one (III) in an 86% yield. The reactivity of this intermediate (Id) to carbonyl compounds was then examined.

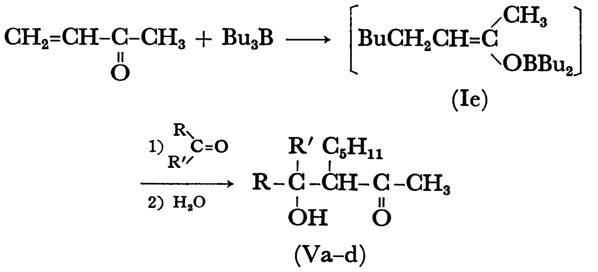


$$\mathrm{CH_2{=}CH\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_3} + \mathrm{Bu_2B\text{-}S\text{-}C_6H_5} \longrightarrow \left[\mathrm{C_6H_5\text{-}SCH_2\text{-}CH{=}C}\begin{smallmatrix}\diagup \mathrm{CH_3}\\ \diagdown \mathrm{OBBu_2}\end{smallmatrix}\right] \xrightarrow{\mathrm{H_2O}} \mathrm{C_6H_5\text{-}SCH_2CH_2\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_3}$$

(II) (Id) (III)

When Id was allowed to react with various carbonyl compounds in dry ether at room temperature, the corresponding *β*-hydroxy-α-(phenylthiomethyl)-ketones (IVa—c) were obtained in fairly good yields. The results are summarized in Table 1. This reaction proceeds in a mode similar to that with other vinyloxyboranes (Ia—c) described in a previous paper.[2)]

Similarly, the vinyloxyborane (Ie), prepared from methyl vinyl ketone and tri-*n*-butylborane according to the method of Suzuki *et al.*,[5)] was caused to react with carbonyl compounds to give *β*-hydroxy-α-*n*-pentyl ketones (Va—d) (Table 1). The reaction of Id, Id′, or Ie with aldehydes gave favorable results, whereas the yields of the products (IVc, Vc, d) were comparatively low when these boranes were treated with ketones.



$$\mathrm{CH_2{=}CH\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_3} + \mathrm{Bu_3B} \longrightarrow \left[\mathrm{BuCH_2CH{=}C}\begin{smallmatrix}\diagup \mathrm{CH_3}\\ \diagdown \mathrm{OBBu_2}\end{smallmatrix}\right] \xrightarrow[2)\ \mathrm{H_2O}]{1)\ \mathrm{RR'C{=}O}} \mathrm{R\text{-}\underset{OH}{\overset{R'}{C}}\text{-}\overset{C_5H_{11}}{CH}\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_3}$$

(Ie) (Va-d)

The addition of a solution of *S*-benzyl diazothioacetate in ether to tri-*n*-butylborane led to the liberation of the nitrogen. On the treatment of the resulting solution with a solution of benzaldehyde or propiophenone in ether, the corresponding α-butyl-*β*-hydroxyalkanethioates were obtained in 51% and 81% yields respectively. The structure of the intermediate was identified as If, in analogy with Ib:

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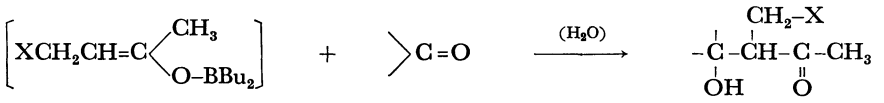
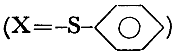
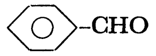
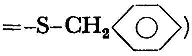
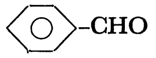
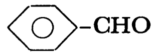
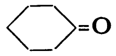
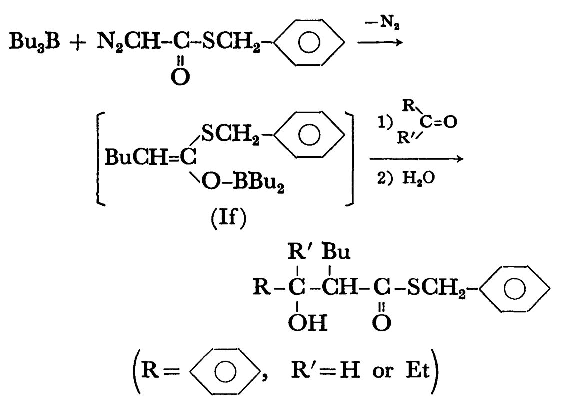
Table 1. Yields of β-hydroxyketone[a]



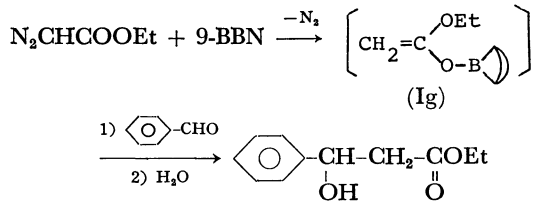
(Id, d′, e) (IVa—d, Va—d)

Vinyloxyboranes	Carbonyl compounds	Reaction time	Products	Isolated yield(%)
Id (X=)		1.5 hr	IVa	93
	n-C_3H_7CHO	1 day	IVb	83
	CH_3COCH_3	3 day	IVc	20[b]
Id′ (X=)		13 hr	IVd	72
Ie (X=n-Bu)		0.5 hr	Va	91
	n-C_3H_7CHO	1 day	Vb	71
	CH_3COCH_3	1 day	Vc	15
		1 day	Vd	38

a) In THF at room temperature. b) Isolated III in 42% yield.

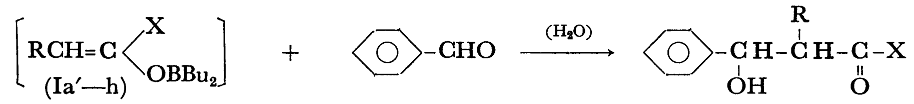


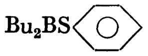
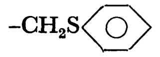
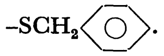
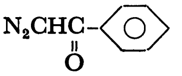
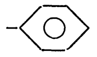
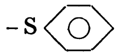
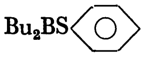
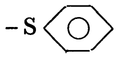
The reaction of ethyl diazoacetate, 9-borabicyclo[3.3.1]nonane (9-BBN), and benzaldehyde were tried in order to know the migrating tendency of the substituents on the boron atom in 9-BBN.[6,7] Ethyl β-hydroxyhydrocinnamate was consequently obtained in a 43% yield by the same procedure as in the case of tri-n-butylborane. It was found that the preferential cleavage of the B–H bond in 9-BBN occurred to form the vinyloxyborane (Ig) as follows:



The experimental results in both the previous and

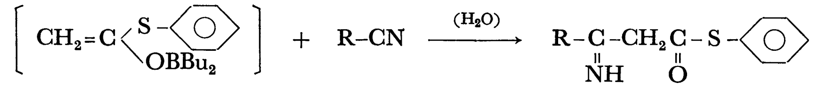
Table 2. Reactions of various vinyloxyboranes with benzaldehyde



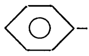
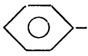
Starting materials			Vinyloxyboranes	(R)	(X)	Isolated yield (%)
$CH_2{=}CH\underset{\underset{O}{\|}}{C}CH_3$	+		Id		CH_3	93[8]
$CH_2{=}CH\underset{\underset{O}{\|}}{C}CH_3$	+	Bu_3B	Ie	$-C_5H_{11}$	CH_3	91
$N_2CHCOOEt$	+	Bu_3B	Ib	Bu	OEt	81[2]
	+	Bu_3B	If	Bu		51
	+	Bu_3B	Ic	Bu		98[2]
$N_2CHCOOEt$	+	9-BBN	Ig[a]	H	OEt	43
$CH_2{=}C{=}O$	+		Ia′	H		96[2]
$CH_3\underset{Br}{CH}{-}COBr$ + Zn	+		Ih	Me		85[8]

a) The substituent group of the boron is not n-butyl but 1,5-cyclooctylene.

TABLE 3. YIELDS OF β-IMINOTHIOATES[a)]



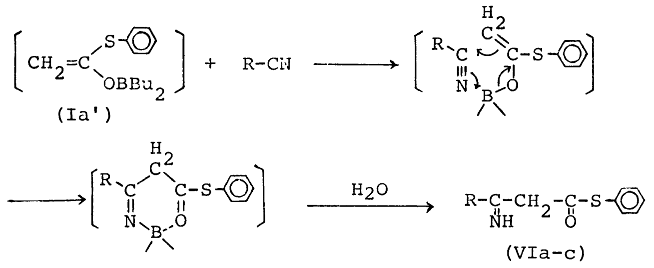
(Ia′) (VIa—c)

Nitriles	Products	Isolated yield (%)
-CN	VIa	37
-CH_2CN	VIb	39
CH_3CN	VIc	35

a) 1 day in ether at room temperature.

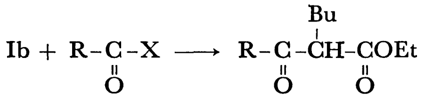
present papers show that vinyloxyboranes (Ia—h: R=H, alkyl, cyclohexyl, or thiomethyl; X=OR, SR, alkyl, or aryl) easily react with carbonyl compounds to afford the corresponding β-hydroxy- esters, thioates, or ketones in good yields. As an example, the reactions of these vinyloxyborane derivatives with benzaldehyde are listed in Table 2.

Next, the reaction of vinyloxyboranes with nitriles was attempted. When vinyloxyborane (Ia′; Ia, R=Ph), prepared from S-phenyl di-*n*-butylthioboronite (II) and ketene, was allowed to react with nitriles at room temperature for 1 day under argon, β-iminothioates (VIa—c) were obtained after hydrolysis (Table 3).



Similarly, Ib reacted with some nitriles to afford α-butyl-β-ketoesters in about 55—70% yields after hydrolysis, as is shown in Table 4.

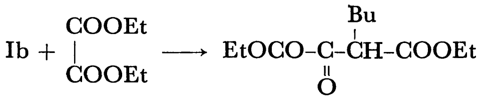
Furthermore, the reactions of Ib with various carboxylic acid derivatives, such as acyl halides, esters, and amides, were examined. Benzoyl bromide and phenylacetyl chloride gave the corresponding β-ketoesters in 31% and 9% yields respectively when they were submitted to a reaction with Ib at room temperature under argon, followed by hydrolyses.



$$\mathrm{Ib} + \mathrm{R{-}\underset{\|}{\overset{}{C}}{-}X} \longrightarrow \mathrm{R{-}C(=O){-}\overset{Bu}{\overset{|}{C}}H{-}C(=O)OEt}$$

It was found that Ib hardly reacts at all with any esters or amides except for formic and oxalic acid derivatives. The borane (Ib) reacted with formic acid derivatives, such as ethyl or *p*-nitrophenyl formate and *N*,*N*-dimethylformamide, to afford ethyl α-formyl-*n*-hexanoate (Table 5). In general, such formyl compounds are prepared by the mixed Claisen condensation of esters and formate in the presence of strong bases. According to the present reaction, however, the formyl compounds are produced under almost neutral conditions.

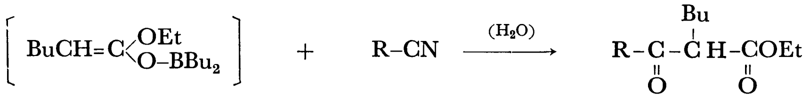
Diethyl oxalate, which is often used in the mixed Claisen condensation, also reacted with Ib at room temperature to give ethyl α-ethoxalylhexanoate in a 46% yield.



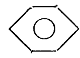
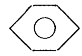
$$\mathrm{Ib} + \begin{array}{c}\mathrm{COOEt}\\ |\\ \mathrm{COOEt}\end{array} \longrightarrow \mathrm{EtOCO{-}C(=O){-}\overset{Bu}{\overset{|}{C}}H{-}COOEt}$$

There are two possible pathways for the reaction of vinyloxyborane with carboxylic acid derivatives: Path (a), similar to that of vinyloxyboranes with carbonyl compounds, and Path (b), accompanied by the initial fission of the C–OR′ or C–NR′$_2$ bond of formate or formamide, as is sketched below:

TABLE 4. YIELDS OF α-BUTYL-β-KETO ESTERS[a)]

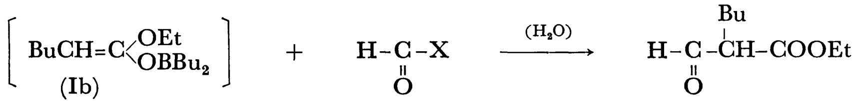


(Ib) (VIIa-d)

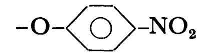
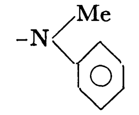
Nitriles	Reaction time	Products	Isolated yield (%)
-CN	16 hr	VIIa	71
-CH_2CN	10 hr	VIIb	61
MeCN	1 day	VIIc	57
n-C_3H_7CN	5 hr	VIId	54

a) In THF at room temperature.

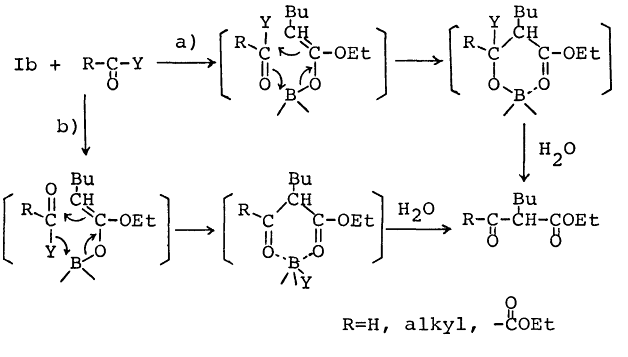
Table 5. Yields of ethyl α-formylhexanoate[a)]



$$\left[\mathrm{BuCH{=}C}\begin{matrix}\mathrm{OEt}\\ \mathrm{OBBu_2}\end{matrix}\right]_{\mathrm{(Ib)}} + \mathrm{H{-}\overset{}{\underset{\displaystyle O}{\underset{\|}{C}}}{-}X} \xrightarrow{(\mathrm{H_2O})} \mathrm{H{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}\overset{\displaystyle Bu}{\overset{|}{C}}H{-}COOEt}$$

Formyl derivatives (X)	Reaction time	Isolated yield (%)
-OMe	16 hr	65
-OEt	13 hr	60
	16 hr	44
-NMe$_2$	1 day	40
	12 hr	8

a) In ether at room temperature.



It should be noted that vinyloxyboranes, which react, under mild conditions, with carbonyl compounds, nitriles, or formates, may be useful as intermediates for the synthesis of a variety of β-hydroxy, β-keto- or α-formyl- ester, thioate, and ketone derivatives.

Experimental[9)]

Materials. Tri-*n*-butylborane was prepared from boron trifluoride diethyl etherate and *n*-butylmagnesium bromide in dry ether under argon. *S*-Phenyl di-*n*-butylthioboronite was prepared from tri-*n*-butylborane and thiophenol at 180 °C.[3)]

Reaction of S-Phenyl Di-n-butylthioboronite and Methyl Vinyl Ketone. To a solution of *S*-phenyl di-*n*-butylthioboronite (235 mg, 1.0 mmol) in CCl_4, we added methyl vinyl ketone (80 mg, 1.1 mmol) at room temperature under argon. After 30 min, the PMR spectrum of the solution was measured to show the formation of a vinyloxyborane (Id). PMR (CCl_4) δ 1.78 (s, 3H), 3.36 (d, J=8 Hz, 2H), 4.77 (t, J=8 Hz, 1H). The solution was then hydrolyzed with aqueous methanol and extracted with ether. The ethereal extracts were washed with water, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was separated by preparative tlc to give 4-phenylthiobutan-2-one (III) in an 86% yield; bp 135—136 °C/8 mmHg. IR 1715, 1580, 1475, 740, 690 cm^{-1}. PMR ($CDCl_3$) δ 2.09 (s, 3H), 2.6—3.3 (m, 4H), 7.32 (s, 5H).

Reaction of Vinyloxyborane (Id) with n-Butyraldehyde. To a solution of (1-methyl-3-phenylthio-1-propenyloxy)di-*n*-butylborane (Id) prepared from *S*-phenyl di-*n*-butylthioboronite (319 mg, 1.4 mmol) and methyl vinyl ketone (100 mg, 1.4 mmol) in ether, we added a solution of butyraldehyde (94 mg, 1.3 mmol) in abs. ether (1 ml). The mixture was allowed to stand overnight and concentrated, and the residue was treated with water and bubbled air for 1 hr and then further extracted with ether. The ethereal layers were washed successively with 5% $NaHCO_3$ and H_2O, dried over Na_2SO_4, and evaporated. The residual oil was purified by preparative tlc (silica gel/$CHCl_3$) to give the pure oil of 4-hydroxy-3-phenylthiomethylheptan-2-one (IVb); 274 mg (83%); IR 3440, 1695 cm^{-1}. PMR ($CDCl_3$) δ 0.8—1.5 (m, 7H), 2.22 (s, 3H), 2.5 (broad s, 1H), 2.8—3.0 (m, 1H), 3.2 (d, 2H), 3.9 (d, 1H), 7.32 (m, 5H). Found: C, 66.48; H, 8.11; S, 12.79%. Calcd for $C_{14}H_{20}O_2S$: C, 66.62; H, 7.99; S, 12.71%.

The IR and PMR spectra and analysis of the other β-hydroxy-α-thiomethyl ketones (IVa, c, d) are consistent with the assigned structure. IVa; IR 3440, 1700 cm^{-1}. PMR ($CDCl_3$) δ 1.97 (s, 3H), 2.9—3.4 (m, 4H), 4.8—5.0 (m, 1H), 7.17 (s, 5H), 7.30 (s, 5H). Found: C, 70.85; H, 6.53; S, 11.28%. Calcd for $C_{17}H_{18}O_2S$: C, 71.28; H, 6.33; S, 11.19%. IVc; IR 3420, 1695 cm^{-1}. PMR ($CDCl_3$) δ 1.22 (s, 6H), 2.28 (s, 3H), 2.1—2.4 (broad s, 1H), 2.8—3.35 (m, 3H), 7.29 (s, 5H). Found: C, 65.28; H, 7.48; S, 13.32%. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61; S, 13.45%. IVd; IR 3410, 1695 cm^{-1}. PMR ($CDCl_3$) δ 1.88 (s, 3H), 2.6—3.4 (m, 4H), 3.70 (s, 2H), 4.65—4.8 (m, 1H), 7.15 (s, 5H), 7.20 (s, 5H). Found: C, 71.70; H, 6.97; S, 10.88%. Calcd for $C_{18}H_{20}O_2S$: C, 71.97; H, 6.71; S, 10.68%.

Reaction of Vinyloxyborane (Ie) with Benzaldehyde. A solution of methyl vinyl ketone (150 mg, 2.1 mmol) and tri-*n*-butylborane (450 mg, 2.4 mmol) in abs. THF was stirred at room temperature under nitrogen containing a little oxygen overnight to give (1-methyl-1-heptenyloxy)di-*n*-butylborane (Ie). To the solution we then added a solution of benzaldehyde (160 mg, 1.5 mmol) in abs. THF. After 30 min, the solvent was removed. The residue was treated with a mixture of MeOH (20 ml) and 30% H_2O_2 (1 ml) for 1 hr, and further water was added. The mixture was concentrated *in vacuo* to remove the MeOH and extracted with ether. The extracts were washed with 5% $NaHCO_3$ and water, dried over Na_2SO_4, and evaporated. The oil was separated by preparative tlc to give 3-(α-hydroxybenzyl)octan-2-one (Va), both *threo* type (240 mg, 68%) and *erythro*-type (79 mg, 23%). Va of the *threo* type: IR 3420, 1700 cm^{-1}; PMR (CCl_4) δ 0.6—1.8 (m, 11H), 2.06 (s, 3H), 2.73 (m, 1H), 3.32 (s, 1H), 4.56 (d, 1H), 7.23 (s, 5H). Va of the *erythro* type: IR 3420, 1695 cm^{-1}: PMR (CCl_4) δ 0.6—1.8 (m, 11H), 1.83 (s, 3H), 2.70 (m, 1H), 3.15 (s, 1H), 4.70 (d, 1H), 7.23 (s, 5H).

The IR and PMR spectra of the other β-hydroxy-γ-pentylketones (Vb—d) are consistent with the assigned structure.

Vb; IR 3410, 1690 cm^{-1}: PMR (CCl_4) δ 0.7—1.9 (m, 18H), 2.13 (s, 3H), 2.3—2.7 (m, 1H), 3.17 (s, 1H), 3.5—3.9 (m, 1H). Vc; IR 3440, 1690 cm^{-1}: PMR (CCl_4) δ 0.6—1.8 (m, 11H), 1.10 (s, 3H), 1.15 (s, 3H), 2.13 (s, 3H), 2.3—2.9 (m, 2H). Vd; IR 3470, 1685 cm^{-1}: PMR (CCl_4) δ 0.6—2.0 (m, 21H), 2.15 (s, 3H), 2.53 (t, 1H), 2.65 (broad s, 1H).

Reaction of Vinyloxyborane (Ia′) and Benzyl Cyanide. To a solution of *S*-phenyl di-*n*-butylthioboronite (419 mg, 1.8 mmol) in asb. ether (10 ml), we added 45 ml of gaseous ketene (prepared by the thermal cracking of acetone) at −78° under argon. After 10 min, we added benzyl cyanide (174 mg, 1.5 mmol) to the solution of vinyloxyborane (Ia′) at room temperature. The reaction mixture was then allowed to stand for 21 hr and concentrated. MeOH was added to the residue and then, after 12 hr, removed *in vacuo*. The residual oil was separated by preparative tlc to give *S*-phenyl β-imino-γ-phenylbutyrothioate (VIb) 155 mg (39%). Recrystallization from cyclohexane: mp 74.0 °C. IR 3455, 3305, 1615, 1520 cm^{-1}. Found: C, 71.27; H, 5.75; N, 5.02; S, 11.88%. Calcd for $C_{16}H_{15}NOS$: C, 71.36; H, 5.61; N, 5.20; S, 12.14%.

The IR and analyses of the other β-iminothioates (VIa, c) are consistent with the assigned structure. VIa (mp 111—112 °C); IR 3380, 3290, 3200, 1610, 1520 cm^{-1}. Found: C, 70.70; H, 5.10; N, 5.68; S, 12.53%. Calcd for $C_{15}H_{13}NOS$: C, 70.58; H, 5.13; N, 5.49; S, 12.53%. VIc (oil); IR 3410, 3305, 3200, 1607, 1520 cm^{-1}. Found: C, 61.95; H, 6.04; N, 6.96; S, 16.56%. Mol wt, 193 (mass spectrometry). Calcd for $C_{10}H_{11}NOS$: C, 62.16; H, 5.74; N, 7.25; S, 16.51%. Mol wt, 193.2.

Reaction of Vinyloxyborane (Ib) with Benzonitrile. A solution of ethyl diazoacetate (242 mg, 2.1 mmol, dried over P_2O_5) in THF (1 ml) was stirred into a solution of tri-*n*-butylborane (398 mg, 2.1 mmol) in THF (3 ml) at room temperature under argon. N_2 was immediately evolved, and the yellow coloration characteristic of ethyl diazoacetate disappeared. After 5 min, a solution of benzonitrile (108 mg, 1.1 mmol) in THF was added to the solution. The reaction mixture was then allowed to stand at room temperature for 16 hr, after which the solution was treated with a mixture of 5% HCl (2 ml), MeOH (3 ml), and 30% H_2O_2 (1.5 ml) for 4 hr. Water was added to the solution, and the mixture was concentrated *in vacuo* to remove most of the THF and MeOH and extracted with ether. The ether layer was washed with 5% $NaHCO_3$ and satd. NaCl and dried over Na_2SO_4, and the solvent was removed. The crude oil was purified by preparative tlc (silica gel, benzene) to give the pure oil of ethyl α-benzoylhexanoate (VIIa); 184 mg, 71%. IR 1740, 1695 cm^{-1}. PMR (CCl_4) δ 0.65—2.4 (m, 13H), 4.10 (q, J=7 Hz, 2H), 7.4—7.6 (m, 3H), 7.8—8.05 (m, 2H). Found: C, 72.42; H, 8.18%. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12%.

The IR and PMR spectra of the other β-ketoesters (VIIb—d) are consistent with the assigned structure. VIIb; IR 1740, 1715 cm^{-1}; PMR (CCl_4) δ 0.7—2.0 (m, 12H), 3.47 (t, J=6 Hz, 1H), 3.73 (s, 2H), 4.10 (q, J=7 Hz, 2H), 7.17 (s, 5H). VIIc; IR 1740, 1720 cm^{-1}: PMR (CCl_4) δ 0.7—2.4 (m, 13H), 2.17 (s, 3H), 4.10 (q, J=7 Hz, 2H), VIId: IR 1745, 1715 cm^{-1}. PMR (CCl_4) δ 0.6—2.6 (m, 18H), *ca.* 3.2 (m, 2H), 4.08 (q, J=7 Hz, 2H).

Reaction of Vinyloxyborane (Ib) with Ethyl Formate. A solution of ethyl diazoacetate (2.74 g, 24 mmol) in asb. ether (5 ml) was stirred into a solution of tri-*n*-butylborane (3.65 g, 20 mmol) and ethyl formate (1.85 g, 25 mmol) in ether (20 ml) at room temperature under argon. The solution was then allowed to stand at room temperature for 16 hr, and ether was added. The solution was washed with a 5% solution of $NaHCO_3$ and water and then dried over anhydrous Na_2SO_4, after which the solvent was evaporated to give a crude oil. The oil was purified by silica-gel-column chromatography to give the pure oil of ethyl α-formylhexanoate (1.95 g, 60%); bp 88—91 °C/9 mmHg. (lit,[10] bp 94—96 °C/10 mmHg). IR 1740 (shoulder), 1720, 1660 cm^{-1}. Found: C, 62.57; H, 9.45%. Mol wt, 172 (mass spectrometry). Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36%; Mol wt, 172.2.

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