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The Synthesis of *Se*-Alkyl Alkaneselenoates via (1-Iodo-1-alkenyl)dialkylboranes

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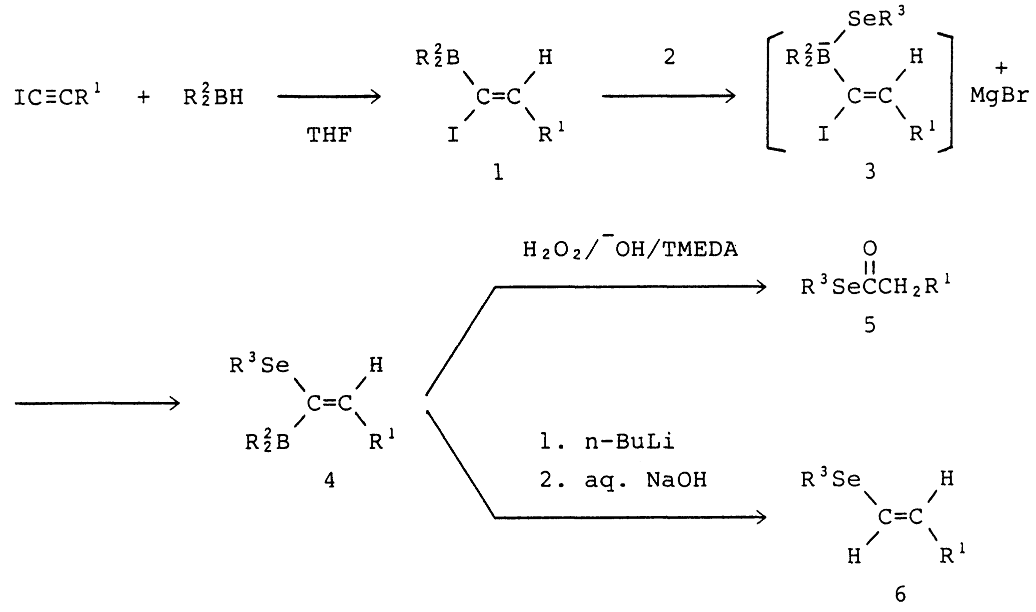
Synopsis. *Se*-Alkyl alkaneselenoates were formed in moderate to good yields by successive reactions of (1-iodo-1-alkenyl)bis(1,2-dimethylpropyl)boranes with alkylselenomagnesium bromides and alkaline hydrogen peroxide.

Se-Alkyl alkaneselenoates (**5**) are receiving considerable attentions in organic syntheses.[1] A synthetic method for **5** has been developed employing carboxylic acid derivatives or selenocarboxylic acid derivatives as the substrates in most cases.[2] In our previous work, the reaction of (1-iodo-1-alkenyl)dialkylboranes (**1**) with alkylthiomagnesium bromides proceeded with inversion of configuration to give (*E*)-(1-alkylthio-1-alkenyl)dialkylboranes, which provided *S*-alkyl alkanethioates on alkaline hydrogen peroxide oxidation.[3] The above results led us to examine the synthesis of (*E*)-(1-alkylseleno-1-alkenyl)dialkylboranes (**4**) and, further, a new synthesis of **5** via **4**.

Preliminarily, (1-iodo-1-hexenyl)bis(1,2-dimethylpropyl)borane (**1a**), prepared by the hydroboration of 1-iodo-1-hexyne with bis(1,2-dimethylpropyl)borane in THF, was treated with an equimolar amount of butylselenomagnesium bromide (**2a**),[4] and the reaction mixture was then oxidized by alkaline hydrogen peroxide in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA). As expected, *Se*-butyl hexaneselenoate (**5a**) was obtained in 58% yield. It was isolated from the oxidized mixture by column chromatography using silica gel (eluted by a mixture of benzene and hexane, 1 : 4). It was then identified by a comparison of its ^{1}H NMR, ^{13}C NMR, IR, and MS spectra with those of an authentic sample prepared by another method.[2a] The yield increased to 95% by employing a two-fold amount of **2a** under the same reaction conditions, though dibutyl selenide and dibutyl diselenide were competitively formed. These contaminants were easily separated from **5a** during the above-mentioned column chromatography. An addition of TMEDA was necessary; otherwise, the yield became nearly zero. A migration of 1,2-dimethylpropyl group from the boron atom to the α-alkenyl carbon atom,[5] a possible side reaction, did not occur under any cases. As shown in Table 1, several types of alkylselenomagnesium bromides may be employed in the present reaction. Thus, in the cases of primary and secondary alkylselenomagnesium bromides, the selenoates **5** were produced in 50—90% yields. The unsatisfactory results, which appeared in the case of 1,1-dimethylethyl-



$$R^3MgBr + Se \longrightarrow R^3SeMgBr \quad \mathbf{2}$$

1a, 3a, 4a, 5a and 6a; R^1 and R^3 =butyl
R^2 =$CH(CH_3)CH(CH_3)_2$

Scheme 1.

Table 1. Yields of *Se*-Alkyl Alkaneselenoates (**5**) and (*E*)-1-Alkylseleno-1-alkenes (**6**)

R^1 of $IC\equiv CR^1$	R^3 of $R^3SeMgBr$	Product and yield/%[a]	
		$R^3SeCOCH_2R^1$[b] (**5**)	(*E*)-$R^3SeCH{=}CHR^1$[c] (**6**)
n-C_4H_9	C_2H_5[d]	80	67
n-C_4H_9	i-C_3H_7	73	80
n-C_4H_9	n-C_4H_9	90	70
n-C_4H_9	s-C_4H_9	75	65
n-C_4H_9	t-C_4H_9	0	—
n-C_4H_9	c-C_6H_{11}	52	42
n-C_4H_9	C_6H_5	33	64
n-C_4H_9	$C_6H_5CH_2$[e]	50	40
n-C_6H_{13}	n-C_4H_9	75	51

a) Based on starting 1-iodo-1-alkyne. b) Isolated. c) Determined by GLC. d) The preparation was carried out at −40 °C. e) The preparation was carried out in diethyl ether at −20 °C.

magnesium bromide, may be attributed to a difficulty regarding the presence of this reagent under the reaction conditions employed.

In a similar manner to the reaction of **1** with alkylthiomagnesium bromides,[3] **4** were suggested to be formed as precursors of **5**. Therefore, the boranes **4** would be expected to provide the corresponding (*E*)-1-alkylseleno-1-alkenes (**6**) on protonolysis of carbon-boron bond. Thus, an attempt to provide (*E*)-1-butylseleno-1-hexene (**6a**) was made by a protonolysis of **4a** with various carboxylic acids. A GLC examination of the protonolyzed mixture failed to show any detectable **6a**. However, a treatment of the same mixture successively with butyllithium and aqueous sodium hydroxide, a method reported by Negishi et al. for the conversion of the carbon–boron bond of alkenylboranes into a carbon–hydrogen bond with retention of configuration,[6] afforded highly pure **6a** in 67% yield, estimated by GLC. Compound **6a**, thus obtained, isomerized very easily to (*Z*)-isomer during the isolation procedure using column chromatography to give a mixture of *E*- and *Z*-isomer (*E*/*Z*=74/26). The *E*-isomer was assigned by an absorption band at 945 cm^{-1} in the IR spectrum and a coupling constant of 15 Hz between olefinic protons in the ^{1}H NMR spectrum. The *Z*-isomer was assigned by a coupling constant of 10 Hz between olefinic protons in the ^{1}H NMR spectrum. In similar reactions, several types of **6** were produced stereoselectively (Table 1); however, they also gave mixtures of *E*- and *Z*-isomer respectively in the isolation process. Thus, the above results strongly suggest an intermediary formation of **4**, though they have not yet been isolated and, thus, have not been directly analyzed. Accordingly, the reaction was speculated to proceed in the following way. Thus, with the alkylseleno anion, the boranes **1** form borate-complexes (**3**) which are transformed to **4** with an inversion of configuration; then, the boranes **4** are converted to **5** and **6**, respectively.

The present reaction not only offers a new synthetic method for *Se*-alkyl alkaneselenoates but also suggests the formation of alkenylboranes having the alkylseleno group on the α-alkenyl carbon atom. These alkenylboranes are expected to be versatile intermediates for various organoselenium compounds.

Experimental

Instruments. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol FX-200 (200 MHz) spectrometer and obtained from a $CDCl_3$ solution containing TMS as the internal standard. IR spectra (film) were recorded with a Hitachi 285 spectrometer. Mass spectra were recorded with a Hitachi M-52 mass spectrometer.

Materials. Commercial 2-methyl-2-butene was purified by distillation over lithium aluminium hydride under an argon stream, and stored under an argon atmosphere. 1-Iodo-1-alkynes were prepared as described in the literature,[7] and used after drying over Molecular Sieves-4A. Commercial alkyl, phenyl, and benzyl bromides were dried with calcium chloride, purified by distillation, and stored over Molecular Sieves-4A under an argon atmosphere. Commercial selenium powder was used after drying in a vacuum desiccator containing phosphorus pentoxide. THF and diethyl ether were distilled over lithium aluminium hydride under argon stream, and stored under an argon atmosphere. TMEDA was purified by vacuum distillation over calcium hydride, and stored under an argon atmosphere. A THF solution of BH_3 was prepared by a method described in the literature.[8] Hexane and benzene, used as eluent for column chromatography, were distilled over sodium.

Representative Procedure. A solution of bis(1,2-dimethylpropyl)borane (10 mmol) in THF was prepared in a 50-ml argon-flushed round-bottom flask, and to the stirred solution was added 2.08 g of 1-iodo-1-hexyne (10 mmol) at −15 °C. The reaction mixture was stirred for 1 h at 0 °C and for additional 1 h at room temperature to complete the reaction. On the other hand, 0.48 g of magnesium turnings (20 mmol) was placed in a 100-ml round-bottom flask; the flask was then flushed with argon. The flask was charged with 20 ml of dry THF, and 2.74 g of butyl bromide (20 mmol) was slowly added to the vigorously stirred solution at room temperature giving a solution of butylmagnesium bromide in THF. After an addition of 40 ml of dry THF, the solution was cooled to −30 °C. Then, 1.58 g of selenium powder (20 mmol) was added through a sample inlet under argon flow to the vigorously stirred suspended solution of butylmagnesium bromide. After stirring for 1 h at −30 °C, the color of the suspension changed from black to cream. The resulting suspension of butylselenomagnesium bromide was further cooled to −50 °C.

The THF solution of (1-iodo-1-hexenyl)bis(1,2-dimethylpropyl)borane in the 50-ml round-bottom flask was then transferred to the suspended solution with a double-ended needle. The reaction mixture was stirred for 1 h at −50 °C and allowed to warm to room temperature. The reaction mixture was then oxidized by a successive addition of 5 ml of TMEDA, 5 ml of 3 mol dm^{-3} aqueous sodium hydroxide and 5 ml of 30% hydrogen peroxide for 1 h at 0 °C. The resulting mixture was extracted with diethyl ether; extract was then washed with brine, and dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator under reduced pressure, and the residue was put on a silica-gel column. The *Se*-butyl hexaneselenoate (2.12 g) was isolated by elution with a mixture of hexane and benzene (4 : 1) (90% yield).

The spectral data of the products are as follows:

***Se*-Ethyl Hexaneselenoate:** ^{1}H NMR ($CDCl_3$) δ=0.80—0.98 (m, 6H), 1.05—1.80 (m, 6H), 2.60 (t, J=7 Hz, 2H), and 2.89 (q, J=7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=13.84, 15.97, 22.30, 25.17, 29.69, 30.98, 48.26, and 202.17 (>C=O); IR (film) 1715 (C=O) cm^{-1}; MS m/z 206 and 208 (M$^+$).

***Se*-(1-Methylethyl) Hexaneselenoate:** ^{1}H NMR δ=0.83—0.96 (m, 3H), 1.20—1.80 (m, 6H), 1.46 (d, J=7 Hz, 6H), 2.57 (t, J=7 Hz, 2H), and 3.50—3.75 (m, 1H); ^{13}C NMR δ=13.86, 22.33, 24.32 (CH_3-, 2C), 25.17, 31.00, 33.22 (>CH-), 48.44, and 202.99 (>C=O); IR 1710 (C=O) cm^{-1}; MS m/z 220 and 222 (M^+).

***Se*-Butyl Hexaneselenoate:** ^{1}H NMR δ=0.82—0.98 (m, 6H), 1.14—1.85 (m, 10H), 2.60 (t, J=7 Hz, 2H), and 2.90 (t, J=7 Hz, 2H); ^{13}C NMR δ=13.57, 13.86, 22.33, 23.09, 25.22 (-CH_2-, 2C), 31.00, 32.64, 48.26, and 202.29 (>C=O); IR 1715 (C=O) cm^{-1}; MS m/z 234 and 236 (M^+).

***Se*-(1-Methylpropyl) Hexaneselenoate:** ^{1}H NMR δ=0.80—1.03(m, 6H), 1.15—1.83 (m, 8H), 1.46 (d, J=7 Hz, 3H), 2.58 (t, J=7 Hz, 2H), and 3.37—3.63 (m, 1H); ^{13}C NMR δ=12.35, 13.86, 22.01, 22.33, 25.22, 30.60, 31.00, 40.58 (>CH-), 48.50, and 202.87 (>C=O); IR 1710 (C=O) cm^{-1} ; MS m/z 234 and 236 (M^+).

***Se*-Cyclohexyl Hexaneselenoate:** ^{1}H NMR δ=0.80—1.00 (m, 3H), 1.10—2.10 (m, 16H), 2.57 (t, J=7 Hz, 2H), and 3.43—3.72 (m, 1H); ^{13}C NMR δ=13.86, 22.33, 25.19, 25.69, 26.77 (-CH_2-, 2C), 31.00, 34.19 (-CH_2-, 2C), 42.16 (>CH-), 48.47, and 202.64 (>C=O); IR 1710 (C=O) cm^{-1} ; MS m/z 260 and 262 (M^+).

***Se*-Phenyl Hexaneselenoate:** ^{1}H NMR δ=0.78—0.98 (m, 3H), 1.10—1.85 (m, 6H), 2.69 (t, J=7 Hz, 2H), and 7.27—7.60 (m, 5H); ^{13}C NMR δ=13.86, 22.30, 25.08, 30.98, 47.50, 126.52 (>C=), 128.79 (-CH=), 129.29 (-CH=, 2C), 135.77 (-CH=, 2C), and 200.39 (>C=O); IR 1730 (C=O), 735, and 690 cm^{-1}; MS m/z 254 and 256 (M^+).

***Se*-Benzyl Hexaneselenoate:** ^{1}H NMR δ=0.80—0.96 (m, 3H), 1.10—1.43 (m, 4H), 1.50—1.70 (m, 2H), 2.62 (t, J=7 Hz, 2H), 4.14 (s, 2H), and 7.25 (s, 5H); ^{13}C NMR δ=13.84, 22.27, 25.11, 28.76, 30.98, 47.85, 126.84 (-CH=), 128.53 (-CH=, 2C), 128.82 (-CH=, 2C), 128.94 (>C=), and 201.56 (>C=O); IR 1710 (C=O), 755, and 695 cm^{-1}; MS m/z 268 and 270 (M^+).

***Se*-Butyl Octaneselenoate:** ^{1}H NMR δ=0.80—1.00 (m, 6H), 1.16—1.88 (m, 14H), 2.60 (t, J=7 Hz, 2H), and 2.89 (t, J=7 Hz, 2H); ^{13}C NMR δ=13.57, 14.07, 22.60, 23.09, 25.22, 25.54, 28.84, 28.93, 31.61, 32.67, 48.32, and 202.20 (>C=O); IR 1710 (C=O) cm^{-1}; MS m/z 262 and 264 (M^+).

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