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Stereoselective synthesis of conjugated alkadienes via the palladium-catalyzed coupling reaction of (*Z*)- or (*E*)-alkenylboranes with (*Z*)- or (*E*)-2-halo-1-(alkylseleno)ethenes

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Abstract

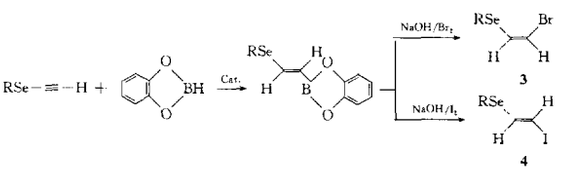
The reaction of (*E*)- or (*Z*)-1-alkenyldicyclohexylboranes (**1** or **2**) with either (*Z*)- or (*E*)-2-halo-1-(alkylseleno)ethenes (**3** or **4**) in the presence of a catalytic amount of tetrakis (triphenylphosphine) palladium and sodium methoxide provides the corresponding (*Z*,*E*)-1-alkylseleno-1,3-alkadienes (**5**, **6** or **7**) with the retention of the configuration from the alkenylboranes and haloalkylselenoethenes. © 1997 Elsevier Science S.A.

Keywords: Alkenylboranes; (Alkylseleno)haloethenes; Palladium; Catalysis; Coupling; Dienyl selenides

1. Introduction

The stereoselective synthesis of conjugated alkadienes is of great importance in organic chemistry because of many natural compounds containing their structural skeletons [1], as well as in their utilization of other reactions such as the Diels–Alder reaction [2]. A number of methods for the preparation of conjugated dienes were previously reported utilizing organometallic compounds [3]. Recently, reports for the synthesis of conjugated functionalized alkadienes have appeared [4,5] (also, for the synthesis of (*E*,*E*)-1,3-alkadienyl selenides, see Ref. [6]). Although various methods for the synthesis of vinylic selenides have been studied intensively [7] (for a review, see also Ref. [8]), the synthesis of conjugated dienyl selenides has been explored little [6].

It is well-known that (*E*)-1-alkenyldicyclohexylboranes **1** is readily prepared by the monohydroboration of terminal alkynes with high stereoselectivity [9]. Similarly, highly pure (*Z*)-1-alkenyldicyclohexylborane **2** is prepared via the monohydroboration of 1-halo-1-alkyne with dicyclohexylborane, followed by treatment with *tert*-butyllithium [10]. On the other hand, we have recently reported regio- and stereoselective synthesis of (*Z*)-2-bromo or (*E*)-2-iodo-1-alkylselenoethenes **3** or **4** by palladium-catalyzed hydroboration of terminal alkylselenoacetylenes, followed by the iodination or bromation under basic conditions [11] (Eq. (1)).



(1)

Consequently, if such 1-alkenyldicyclohexylboranes react with 1-alkylselenoethenyl halides stereoselectively, these reactions provide direct and convenient synthetic procedures for stereodefined conjugated alkadienyl selenides. Although the reaction of alkylboranes with 2-bromo-1-phenylthio-1-alkenes in the presence of $Pd(PPh_3)_4$ and aqueous base was previously reported [12], when such a method was applied to the coupling of alkenylboranes with 2-halo-1-alkylselenoethenes the reaction proceeded with poor stereoselectivity. If basic species such as sodium methoxide are used instead of aqueous base, there may be a possibility that the coupling takes place more readily with high stereoselectiv-

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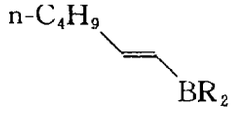
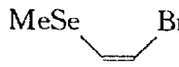
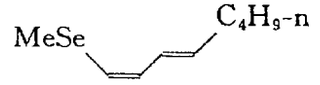
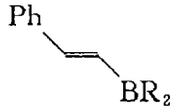
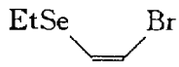
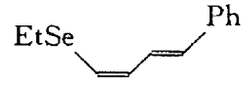
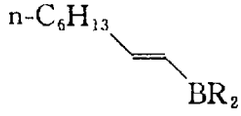
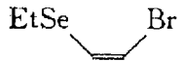
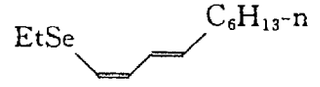
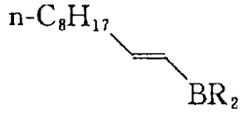
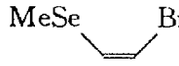
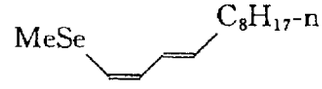
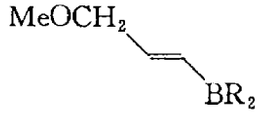
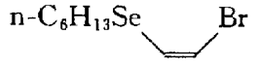
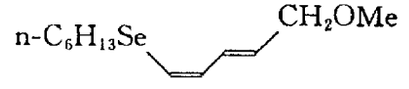
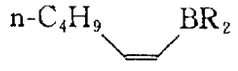
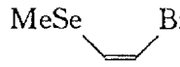
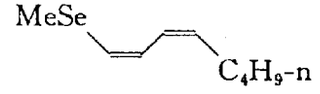
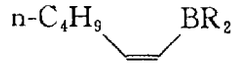
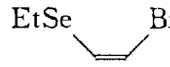
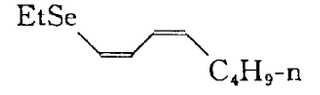
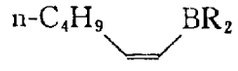
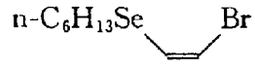
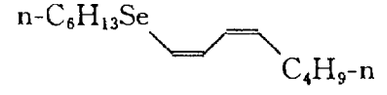
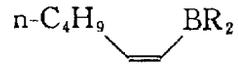
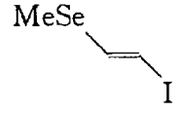
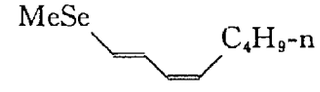
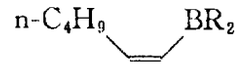
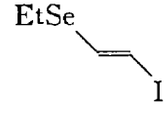
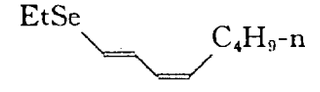
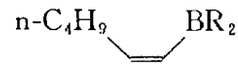
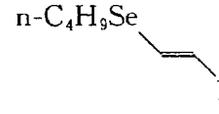
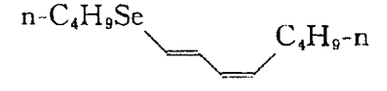
ity. Actually, we found that the reaction proceeded smoothly in the presence of $Pd(PPh_3)_4$ and NaOMe to give the expected conjugated alkadienyl selenides stereoselectively in good to excellent yields. Thus, herein we wish to report a general method for the stereoselective preparation of conjugated alkadienyl selenides.

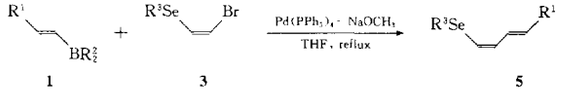
Table 1
The preparation of (*Z*,*E*)-, (*Z*,*Z*)- or (*E*,*Z*)-1,3-alkadienyl selenides

Entry	Alkenylborane	Haloselenoethene	Product	Yield[a] (%)
5a				86
5b				88
5c				84
5d				80
5e				87
6a				73
6b				74
6c				70
7a				85
7b				82
7c				83

[a] Isolated yield of pure compound.

2. Results and discussion

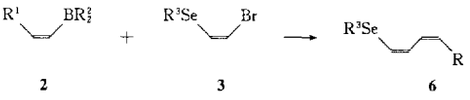
When we attempted to carry out the coupling reaction of (*Z*)-2-bromo-1-methylselenoethene (**3a**) with (*E*)-hexenydicyclohexylborane (**1a**), prepared by the hydroboration of 1-hexyne with dicyclohexylborane, in the presence of a catalytic amount (5 mol%) of Pd $(PPh_3)_4$ and aqueous sodium hydroxide (3 equiv.), it failed in obtaining dienyl selenide in a satisfactory yield, as Suzuki and coworkers described previously [3,5,13], although they reported an interesting stereoselective coupling reaction of alkenyl–thioalkenyl, alkyl–thioalkenyl and alkenyl–alkenyl moieties under the condition described above. However, we found that the reaction mixture took place dramatically, resulting in a clean coupling of carbon–carbon to give (*Z,E*)-1-methylseleno-1,3-octadiene **5a** with high stereoselectivity [14] when NaOMe without any HOMe was used instead of that aqueous base. [1] The syntheses of (*Z,E*)-1-alkylseleno-1,3-alkadienes (**5b–e**) were also examined by the cross-coupling of (*Z*)-2-bromo-1-alkylselenoethenes (**3b–e**) with the (*E*)-alkenydicyclohexylboranes (**1b–e**) (Eq. (2)). The results are listed in Table 1.



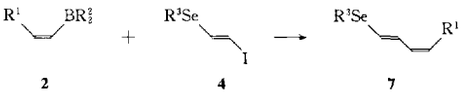
1 3 5 (2)

The results of **5**, summarized in Table 1, showed that (*Z,E*)-1-alkylseleno-1,3-alkadienes were obtained in good yields when NaOMe without any HOMe was used instead of aqueous sodium hydroxide, and the reaction proceeded under mild conditions with high stereoselectivity in which the cross-coupling occurred superiorly at the bromine position instead of the seleno group position.

The (*Z*)-hexenyldicyclohexylboranes **2** can easily be prepared by the hydroboration of 1-bromohexyne with dicyclohexylborane followed by its treatment with *tert*-butyllithium [10]. Thus, we also examined the coupling reaction of (*Z*)-2-bromo-1-alkylselenoethenes **3** with (*Z*)-hexenyldicyclohexylboranes **2** in order to check the utility of the present method for the synthesis of (*Z,Z*)-1,3-hexadienyl selenides. The experimental results showed that the conjugated (*Z,Z*)-1,3-octadienyl selenides **6** can be synthesized under the reaction condition analogous to the synthesis of (*Z,E*)-1,3-alkadienyl selenides **5** with the retention of the configuration from both the starting alkenylboranes and bromoselenoethenes (Eq. (3)). The similar cross-coupling reaction of (*E*)-2-iodo-1-alkylselenoethenes **4** with (*Z*)-hexenyldicyclohexylboranes **2** under the same conditions gave (*E,Z*)-1-alkylseleno-1,3-octadienes **7** (Eq. (4)). All results are summarized in Table 1. These results also indicated that the Pd(O)-catalyzed coupling of alkenyl-selenoalkenyl proceeds smoothly under refluxing in the presence of $NaOCH_3$ with high stereoselectivity.



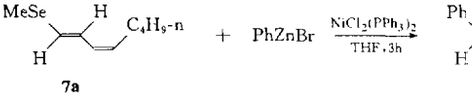
2 3 6 (3)



2 4 7 (4)

The stereochemistry of compounds **5**, **6** or **7** was established from the characteristic coupling constant of the (*Z*)- or (*E*)-configuration between two olefinic proton signals in the ^1H NMR spectrum. For example, in the case of **5b**, one olefinic proton signal at δ 5.95 or 6.27 ppm was split into a characteristic coupling constant ($J = 9.5$ Hz) of the (*Z*)-configuration, while one olefinic proton signal at δ 6.46 or 6.88 ppm had a characteristic coupling constant ($J = 14.5$ Hz) of the (*E*)-configuration.

We also tried to carry out the coupling reaction of compound **7a** at room temperature in THF with phenylzinc bromide [12] in the presence of 5 mol% of $NiCl_2(PPh_3)_2$ for 3 h to give **8** in isolated yield of 83% (Eq. (5)); the result corresponded with that reported in the literature [3] and indicates that the coupling reaction takes place readily with the retention of configuration.



7a 8 (5)

By this methodology, we first report a general route to the synthesis of (1*Z*,3*E*)-, (1*Z*,3*Z*)- or (1*E*,3*Z*)-dienyl selenides by a Pd(O)-catalyzed coupling reaction of alkenylboranes with alkylselenoethenyl halide. The investigation on the synthetic applications of these dienyl selenides is in progress.

3. Experimental details

IR spectra were obtained as films on a Shimadzu IR-435 spectrometer. ^1H NMR spectra (chemical shifts in parts per million from internal TMS) were measured on a Bruker AC-P200 (200 MHz) spectrometer with $CDCl_3$ as solvent. MS was determined by an HP-5890A spectrometer. Elemental analyses were conducted using a Yanaco MT-3 CHN elemental analyzer. All reactions were carried out under a stream of dry nitrogen. All solvents were dried, deoxygenated and redistilled before

[1] Sodium methoxide was obtained according to the literature [14].

use. (*E*)-Alkenyldicyclohexylboranes [9], (*Z*)-alkenyldicyclohexylboranes [10], NaOMe [14], phenylzinc bromide [12] and $Pd(PPh_3)_4$ [15] were prepared according to known methods. The borane was made in the laboratory according to the method reported by Brown and Tierney [16]. Commercial sodium borohydride and *tert*-butyllithium were used without purification.

*3.1. General procedure for the synthesis of (Z,E)-1-alkylseleno-1,3-alkadienes (**5a–e**)*

A dry 50 ml flask equipped with a magnetic stirring bar, a septum inlet, an oil bubbler, and a reflux condenser was charged with $Pd(PPd_3)_4$ (0.174 g, 0.15 mmol), dry THF (5 ml) and (*Z*)-2-bromo-1-alkylselenoethene (5 mmol) under nitrogen. The mixture was stirred for 20 min at room temperature, and then to the mixture was added (*E*)-alkenyldicyclohexylborane (5 mmol) in THF (6.25 ml) and NaOMe (0.81 g, 15 mmol). The mixture was refluxed for 4 h. After the reaction was completed and the mixture was cooled down to room temperature, the reaction mixture was diluted with pentane (30 ml), and the organic phase was separated, the extract was dried over $MgSO_4$. After the removal of solvent, product was isolated by chromatography over silica gel with petroleum (b.p. 60–90 °C) to give **5a–e** as an oil.

*3.1.1. (Z,E)-1-Methylseleno-1,3-octadiene (**5a**)*

IR (neat) ν (cm^{-1}): 1657, 1649, 955, 691. ^1H NMR: δ 6.21–6.63 (m, 3 H), 5.85 (dt, 1 H, J = 14.8, 7.1 Hz), 2.20 (s, 3 H), 1.95–2.30 (m, 2 H), 1.15–1.50 (m, 4 H), 0.81 (t, 3 H, J = 6.1 Hz). MS m/z: 204 ($M^+ + 1$). Anal. Found: C, 52.94; H, 8.11. $C_9H_{16}Se$ calc.: C, 53.20; H, 7.94.

*3.1.2. (Z,E)-1-Ethylseleno-4-phenyl-1,3-butadiene (**5b**)*

IR (neat) ν (cm^{-1}): 1664, 1652, 959, 705. ^1H NMR: δ 7.15–7.50 (m, 5 H), 6.88 (d, 1 H, J = 14.5 Hz), 6.46 (dd, 1 H, J = 14.5, 8.2 Hz), 6.27 (dd, 1 H, J = 9.5, 8.2 Hz), 5.95 (d, 1 H, J = 9.5 Hz), 2.88 (q, 2 H, J = 7.8 Hz), 1.60 (t, 3 H, J = 7.8 Hz). MS m/z; 238 ($M^+ + 1$). Anal. Found: C, 60.41; H, 6.29. $C_{12}H_{14}Se$ calc.: C, 60.76; H, 5.95.

*3.1.3. (Z,E)-1-Ethylseleno-1,3-decadiene (**5c**)*

IR (neat) ν (cm^{-1}): 1659, 1655, 964, 687. ^1H NMR: δ 6.59 (dd, 1 H, J = 15, 8.1 Hz), 6.30 (dd, 1 H, J = 10, 8.1 Hz), 6.11 (d, 1 H, J = 10 Hz), 5.81 (dt, 1 H, J = 15, 7.2 Hz), 2.91 (q, 2 H, J = 7.9 Hz), 1.90–2.30 (m, 2 H), 1.59 (t, 3H, J = 7.9 Hz), 1.10–1.53 (m, 8 H), 0.76 (t, 3 H, J = 5.7 Hz). MS m/z: 246 ($M^+ + 1$). Anal. Found: C, 59. 03; H, 9.45. $C_{12}H_{22}Se$ calc: C, 58.76; H, 9.04.

*3.1.4. (Z,E)-1-Methylseleno-1,3-dodecadiene (**5d**)*

IR (neat) ν (cm^{-1}): 1661, 1653, 974, 718. ^1H NMR: δ 6.19–6.56 (m, 3 H), 5.79 (dt, 1 H, J = 14.7, 7 Hz), 1.90–2.28 (m, 2 H), 2.19 (s, 3 H), 1.0–1.55 (m, 12 H), 0.73 (t, 3 H, J = 6.2 Hz). MS m/z: 260 ($M^+ + 1$). Anal. Found: C, 59.89; H, 9.62. $C_{13}H_{24}Se$ calc.: C, 60.22; H, 9.33.

*3.1.5. (Z,E)-5-Methoxyl-1-hexylseleno-1,3-pentadiene (**5e**)*

IR (neat) ν (cm^{-1}): 1672, 1660, 961, 695. ^1H NMR: δ 6.73 (dd, 1 H, J = 14.2, 8.1 Hz), 6.34 (dd, 1 H, J = 9.5, 8.1 Hz), 6.10 (d, 1 H, J = 9.2 Hz), 5.95 (dt, 1 H, J = 7.7 Hz), 3.91 (d, 2 H, J = 6.8 Hz), 3.30 (s, 3 H), 2.85 (t, 2 H, J = 7.7 Hz), 1.57 (m, 2 H), 1.28–1.55 (m, 6 H), 0.91 (t, 3 H, J = 5.7 Hz). MS m/z: 262 ($M^+ + 1$). Anal. Found: C, 54.86; H, 8.11. $C_{12}H_{22}OSe$ calc.: C, 55.17; H, 8.49.

*3.2. General procedure for the synthesis of (Z,Z)-1-alkylseleno-1,3-octadienes (**6a–c**)*

As described for (**5**), (*Z*)-hexenyldicyclohexylborane (5 mmol) in THF (5 ml) and NaOMe (0.81 g, 15 mmol) were allowed to react with a mixture of $Pd(PPh_3)_4$ (0.174 g, 0.15 mmol) and (*Z*)-2-bromo-1-alkylselenoethene (5 mmol) in THF (5 ml). Chromatographic separation over silica gel with petroleum (b.p. 60–90 °C) of crude product afforded **6a–c** as an oil.

*3.2.1. (Z,Z)-1-Methylseleno-1,3-octadiene (**6a**)*

IR (neat) ν (cm^{-1}): 1657, 1641, 735, 729. ^1H NMR: δ 6.26–6.61 (m, 3 H), 5 62 (dt, 1 H, J = 10, 7.2 Hz), 2.18 (s, 3 H), 1.97–2.35 (m, 2 H), 1.15–1.50 (m, 4 H), 0.83 (t, 3 H, J = 6.2 Hz). MS m/z: 204 ($M^+ + 1$). Anal. Found: C, 53.61; H, 8.26. $C_3H_{15}Se$ calc.: C, 53.20; H, 7.94.

*3.2.2. (Z,Z)-1-Ethylseleno-1,3-octadiene (**6b**)*

IR (neat) ν (cm^{-1}): 1651, 1640, 738, 721. ^1H NMR: δ 6.28, 6.64 (dd, 1 H, J = 10, 8.3 Hz), (dd, 1 H, J = 10.5, 8.3 Hz), 6.05 (d, 1 H, J = 10.5 Hz), 5.57 (dt, 1 H, J = 10, 7 Hz), 2.91 (q, 2 H, J = 8 Hz), 1.95–2.32 (m, 2 H), 1.67 (t, 3 H, J = 8 Hz), 1.10–1.50 (m, 4 H), 0.79 (t, 3 H, J = 6.1 Hz). MS m/z: 218 ($M^+ + 1$). Anal. Found: C, 55.07; H, 8.77. $C_{10}H_{18}Se$ calc.: C, 55.30; H, 8.35.

*3.2.3. (Z,Z)-1-Hexylseleno-1,3-octadiene (**6c**)*

IR (neat) ν (cm^{-1}): 1649, 1641, 735, 718. ^1H NMR: δ 6.58 (dd, 1 H, J = 10, 8 Hz), 6.24 (dd, 1 H, J = 9.5, 8 Hz), 6.03 (d, 1 H, J = 9.5 Hz), 5.61 (dt, 1 H, J = 10, 7 Hz), 2.88 (t, 2 H, J = 7.9 Hz), 1.95–2.31 (m, 2 H), 1.61 (m, 2 H), 1.05–1.55 (m, 10 H), 0.93 (t, 3 H, J = 6.7 Hz), 0.75 (t, 3 H, J = 6.2 Hz). MS m/z: 274

($M^+ + 1$). Anal. Found: C, 61.97; H, 9.24. $C_{14}H_{26}Se$ calc.: C, 61.52; H, 9.59.

3.3. General procedure for the synthesis of (E,Z)-1-alkylseleno-1,3-octadienes (7a–c)

As described for (**5**), into a dry 50 ml flask was placed $Pd(PPh_3)_4$ (0.174 g, 0.15 mmol), dry THF (5 ml), and (*E*)-1-iodo-alkylselenoethene. After the mixture was stirred for 20 min, (*Z*)-hexenyldicyclohexylborane (5 mmol) in THF (5 ml) and NaOMe (0.81 g, 15 mmol) were added. Crude product was separated by chromatography over silica gel with petroleum (b.p. 60–90 °C) to give **7** as an oil.

3.3.1. (E,Z)-1-Methylseleno-1,3-octadiene (7a)

IR (neat) ν (cm^{-1}): 1671, 1646, 975, 728. ^1H NMR: δ 6.94 (dd, 1 H, J = 15.5, 9 Hz), 6.27–6.51 (m, 2 H), 5.56 (dt, 1 H, J = 10, 7.2 Hz), 2.21 (s, 3 H), 1.90–2.31 (m, 2 H), 1.20–1.55 (m, 4 H), 0.86 (t, 3 H, J = 5.7 Hz). MS m/z: 204 ($M^+ + 1$). Anal. Found: C, 53.51; H, 7.69. $C_9H_{16}Se$ calc.: C, 53.20; H, 7.94.

3.3.2. (E,Z)-1-Ethylseleno-1,3-octadiene (7b)

IR (neat) ν (cm^{-1}): 1667, 1655, 972, 733. ^1H NMR: δ 6.97 (dd, 1 H, J = 15.5, 9.5 Hz), 6.42 (dd, 1 H, J = 10, 9.5 Hz), 6.21 (d, 1 H, J = 15.5 Hz), 5.51 (dt, 1 H, J = 10, 7.1 Hz), 2.91 (q, 2 H, J = 7.9 Hz), 1.95–2.30 (m, 2 H), 1.62 (t, 3 H, J = 7.9 Hz), 1.15–1.50 (m, 4 H), 0.78 (t, 3 H, J = 6 Hz). MS m/z: 218 ($M^+ + 1$). Anal. Found: C, 54.97; H, 8.04. $C_{10}H_{18}Se$ calc.: C, 55.26; H, 8.41.

3.3.3. (E,Z)-1-Butylseleno-1,3-octadiene (7c)

IR (neat) ν (cm^{-1}): 1675, 1648, 963, 727. ^1H NMR: δ 6.89 (dd, 1 H, J = 15, 9.5 Hz), 6.47 (dd, 1 H, J = 10.5, 9.5 Hz), 6.19 (d, 1 H, J = 15 Hz), 5.60 (dt, 1 H, J = 10.5, 7 Hz), 2.85 (q, 2 H, J = 7.7 Hz), 1.90–2.25 (m, 2 H), 1.65 (m, 2 H), 1.10–1.55 (m, 6 H), 0.97 (t, 3 H, J = 6.7 Hz), 0.81 (t, 3 H, J = 6.2 Hz). MS m/z: 246 ($M^+ + 1$). Anal. Found: C, 59.01; H, 8.77. $C_{12}H_{22}Se$ calc.: C, 58.77; H, 9.04.

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