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A Useful Synthesis of α,β-Bis(methylseleno)alkanes and α,δ-Bis(methylseleno)alk-2-enes by the Reactions of Alkenes and 1,3-Dienes with $B(SeMe)_3$-Lewis Acid

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ABSTRACT

Reactions of tris(methylseleno)borane-$SnCl_4$ with alkenes **1a–g** *gave α,β-bis(methylseleno)alkanes* **2a–g**, *stereospecifically, and reactions with 1,3-dienes* **1i–k** *afforded α,δ-bis(methylseleno)alk-2-enes* **2i–k**, *regioselectively.*

Organoselenoboranes are versatile tools as useful precursors of selenolate anions for selenoacetalization [1] and for the C–O bond cleavage of cyclic ethers [2]. We have recently reported that phenylseleno and methylseleno radicals generated by $B(SeR)_3$-O_2(or AIBN) added to acetylenes but did not add to alkenes effectively [3]. Usually, addition of selenium-centered radicals to alkynes and allenes is successful but addition to alkenes is unsuccessful. Sonoda et al. succeeded in the photochemical thioselenation of alkenes with a mixture of diphenyl disulfide and diphenyl diselenide [4], and Hevesi et al. accomplished the electrophilic 1,2-addition of the methylseleno group to alkenes using dimethyl diselenide and $SnCl_4$ [5]. Recently, we found that tris(methylseleno)-borane reacts with alkenes in the presence of a Lewis acid to afford α,β-bis(methylseleno)alkanes, and we now report reactions of the selenoborane-$SnCl_4$ complex with various alkenes and dienes.

RESULTS AND DISCUSSION

First, we performed reactions of alkenes with $B(SeMe)_3$-$SnCl_4$. The reaction with cyclohexene gave *trans*-1,2-bis(methylseleno)cyclohexane (**2a**) in quantitative yield (entry 1) [5]. Other alkenes and dienes were similarly treated with $B(SeMe)_3$-$SnCl_4$, and the results are shown in Table 1. The reaction of 1-methylcyclohexene (**1c**) gave *trans*-1,2-bis(methylseleno)-1-methylcyclohexane (**2c**) (38%) stereoselectively, accompanied by 1-methyl-1-methylselenocyclohexane (**3c**) (26%). The stereochemistry of bis(selenide) **2c** was determined by ^1H NMR spectroscopy. The 2-H signal was observed at δ 3.13 (dd, J = 3 and 12 Hz). The J values correspond to an axial-equatorial and an axial-axial coupling constant of a cyclohexane ring, respectively, and therefore 2-H occupies the axial position. Nuclear Overhauser effect difference spectroscopy indicates that 2-H and 1-Me are not proximate. The conformation of the functional groups is 1-Me (ax), 1-SeMe (eq), and 2-SeMe (eq).

Since this addition reaction proceeded in an antistereospecific manner, we examined reactions of *trans*-2-heptene (**1d**) and the *cis*-congener **1e** and obtained a single stereoisomer **2d** and its diastereomer **2e**, respectively (entries 4 and 5). The stereochemistry of these diastereomers was deter-

Dedicated to Prof. Shigeru Oae on the occasion of his Seventy-fifth birthday.

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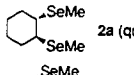
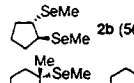
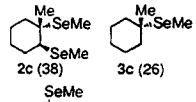
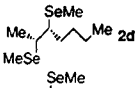
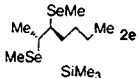
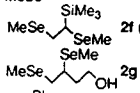
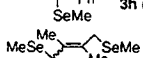
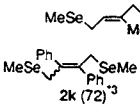
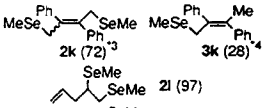
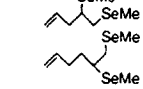
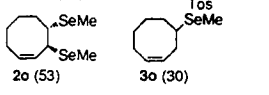
TABLE 1 Reactions of Alkenes and Dienes with $B(SeR)_3$-$SnCl_4$

Entry	Alkenes	Reagents (Molar Ratio to Alkene) $B(SeMe)_3$/$SnCl_4$ and Temperature	Products (% Yield)
1	 1a	1eq./2eq./-40 °C	 2a (quant.)
2	 1b	1eq./2eq./-40 °C	 2b (56)
3	 1c	1eq./2eq./-40 °C	 2c (38) 3c (26)
4	 1d	1eq./2eq./-40 °C	 2d (100)
5	 1e	1eq./2eq./-40 °C	 2e (66)
6	 1f	1eq./2eq./-40 °C	 2f (quant.)
7	 1g	1eq./2eq./-40 °C	2g (33)
8	 1h	1eq./2eq./-40 °C	 3h (26)
9	 1i	1eq./2eq./-40 °C	2i (55)*1 3i (16)
10	 1j	1eq./2eq./-40 °C	 2j (32)*2
11	 1k	1eq./2eq./-40 °C	 2k (72)*3 3k (28)*4
12	 1l	1eq./2eq./-40 °C	 2l (97)
13	 1m	1eq./2eq./-40 °C	2m (88)
14	$TosN(CH_2C{=}CH_2)_2$ 1n	2eq./4eq./-40 °C	 2n (50) 3n (20)
15	 1o	1eq./2eq./-40 °C	2o (53) 3o (30)
16	 1p	1eq./2eq./-40 °C	Complex mixture

*1: E:Z = 1:1; *2: E only; *3: E:Z = 92:8; *4: E only.

mined by the ^1H NMR chemical shift of the 1-Me group. The chemical shift of the *threo*-methyl group is known to be upfield to that of the *erythro*-isomer [6]. The 1-Me signal of **2e** was observed in the upper field by 0.08 ppm as against that of **2d**. The coupling constants J_{2H-3H} of **2d** and **2e** were 5 and 3 Hz, respectively. From this ^1H NMR spectral evidence, **2d** is *erythro*-2,3-bis(methylseleno)heptane and **2e** is the *threo*-isomer. Vinylsilane (**1f**) and 4-buten-1-ol (**1g**) also gave the bis(selenides) **2f** and **2g**, respectively, in good yields. The bulky olefin **1h** afforded the mono selenide **3h** in low yield.

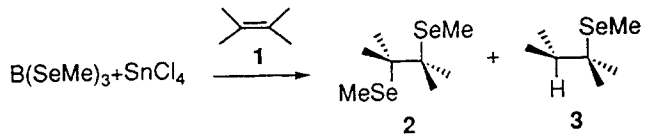
We similarly examined the addition reaction of $B(SeMe)_3$-$SnCl_4$ to 1,3-dienes. The reaction of 2,3-dimethyl-1,3-butadiene (**1i**) with $B(SeMe)_3$-$SnCl_4$ afforded a 1,4-adduct **2i** (E:Z = 1:1) regioselectively, accompanied by the mono selenide **3l** (entry 9). The 1,4-adduct **2k** (E:Z = 92:8) and the monoselenide (E)-**3k** were similarly obtained from the reaction of 2,3-diphenyl-1,3-butadiene (**1k**). The stereochemistry of the products **2k** and **3k** was determined by the ^1H NMR observation that the methylene signals of (E)-**2k** and **3k** were at δ 3.37 and 3.42, respectively, higher field than that of (Z)-**2k** at δ 3.37 because of the shielding effect of the *cis*-phenyl group [7]. 1,4- **1l** and 1,5-Alkadiene **1m** gave 1,2-bis(selenide) **2l** and **2m** in high yields, respectively (entries 12 and 13). When this addition reaction was applied to the diene cyclization of **1n**, we expected the formation of a piperidine derivative. However, the products were tetrakis(methylseleno)alkane **2n** and bis(methylselenide) **3n** in good yields, and the cyclized product was not detected. 1,3-Cyclooctadiene (**1o**) afforded 1,2-adduct **2o** and the monoselenide **3o**, while 1,5-cyclooctadiene gave a complex mixture (entries 15 and 16).

Hevesi et al. have not obtained mono selenides, but we isolated them from some reactions. A reaction pathway via the radical addition of a methylseleno group to a double bond is ruled out because of the regioselective introduction of the methylseleno group to methylcyclohexene (entry 3). α-Ketoselenides [8] or β-haloselenides [9] suffer from the deselenylation by treatment with a selenolate ion. If methaneselenolate ion in the reaction mixture were to attack at the selenide, a mono selenide and dimethyl diselenide would be formed. We examined the reaction of methaneselenolate ion with bis(selenide) **2k** but could not observe formation of the mono selenide **3**.

In order to characterize the reactive reagent, we measured the ^1H and ^{13}C NMR spectra of the reaction mixture of tris(methylseleno)borane with 0.5 equiv of $SnCl_4$ in $CDCl_3$ at -40°C. The ^1H NMR spectrum showed a singlet at δ 2.51 due to the methylseleno group, which was shifted to a considerably lower field than that of tetrakis(methylseleno)tin at δ 2.09. This indicates that the product should contain chlorine atoms. The mixtures of the compounds $Cl_{4-x}Sn(SeMe)_x$ (x = 1–3) showed a single methylseleno resonance, but only time-averaged signals of these compounds were observed [10]. Therefore, we could not specify the origin of the signal of the reaction intermediate.

The stereospecificity and reactivity observed in the α,β-diselenylation of alkenes with tris(methylseleno)borane-$SnCl_4$ are similar to those observed in the diselenylation with dimethyl diselenide-$SnCl_4$, which is initiated by an electrophile "$MeSe^+$". However, the details of the reaction mechanism are not clear at the present stage.

Next, we examined whether the 1,4-methylseleno groups of 1,4-bis(methylseleno)alk-2-enes could be changed to other functional groups. The methylation reaction of **2k** with various bases and MeI (Scheme 2) gave the diene **1k** but no methylated



SCHEME 1

selenides. The reaction of **2k** (*E*:*Z* = 11:1) with NBS afforded dibromide **5** (*E*:*Z* = 5:1) in 67% yield. The product **5** would be formed by the ligand coupling within dibromoselenurane **4**.

EXPERIMENTAL

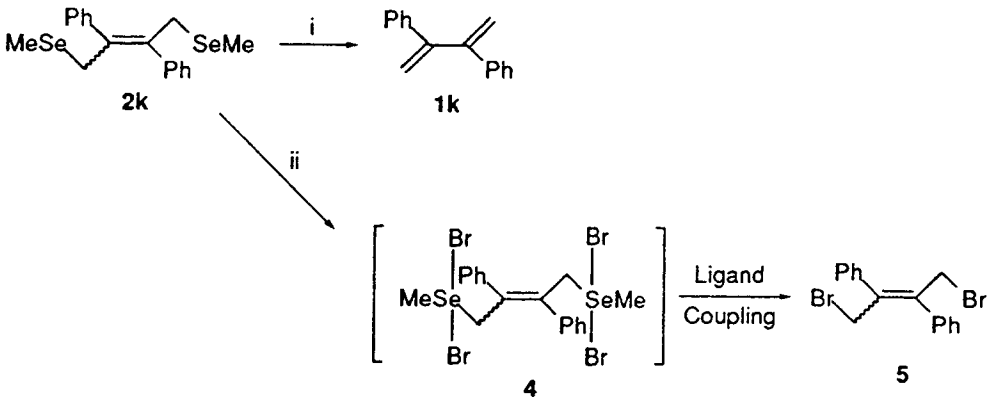
Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra of solids (KBr) and liquids (film) were recorded on a JASCO IRA-100 spectrophotometer. ^{1}H NMR spectra were obtained for solutions in $CDCl_3$ on Hitachi R-20B (60 MHz), JEOL GX-270 (270 MHz), and JEOL EX-400 (400 MHz) spectrometers with tetramethylsilane as an internal standard, unless otherwise indicated. ^{13}C NMR spectra were run on JEOL GX-270 and EX-400 spectrometers. Mass spectra (MS) were recorded by a JEOL JMS-D300 spectrometer with a direct-insertion probe at 70 eV. Exact mass determination was done with a JMA 2000 on-line system. Elemental analyses were performed in the laboratory of elemental analysis of this university.

Typical Procedure for Reactions of B(SeMe)$_3$-SnCl$_4$ with Alkenes and Dienes

trans-1,2-Bis(methylseleno)cyclohexane (**2a**). Cyclohexene (0.10 mL, 1.0 mmol) was added to a CH_2Cl_2 (2 mL) solution of $B(SeMe)_3$ (0.29 g, 1.0 mmol) at −40°C under an Ar atmosphere. $SnCl_4$ (0.24 mL, 2.0 mmol) was added dropwise to the reaction mixture. The whole was warmed to room temperature and poured into sat. $NaHCO_3$ solution (150 mL). The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel with hexane. The title compound (0.27 g, quant.) was obtained as a pale yellow oil (bp 230–240°C/5 mmHg). IR (film) cm^{-1}: 3000, 2925, 2850, 1440, 1360, 1320, 1280, 1200, 1180, 1160, 1000, 980, 900, 860, 840, 820, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$-TMS δ) 0.78–0.84 (2H, m, alkyl H), 1.07–1.08 (4H, m, alkyl H), 1.40 (6H, s, SeMe), 1.58–1.66 (2H, m, alkyl H), 2.47–2.49 (2H, m, CHSe). ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 3.80 (q × 2), 24.96 (t × 2), 32.04 (t × 2), 44.53 (d × 2). Anal. calcd for $C_8H_{16}Se_2$: C, 35.57; H, 5.97; found, C, 35.32; H, 5.91%.

trans-1,2-Bis(methylseleno)cyclopentane (**2b**) (*0.14 g, 56%*). Results by IR (film), 2975, 2950, 2875, 1440, 1420, 1310, 1270, 1140, 1030, 900, 730, 660 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$-TMS δ) 1.69–1.81 (4H, m, alkyl H), 2.03 (6H, s, SeMe), 2.24–2.30 (2H, m, alkyl H), 3.26–3.29 (2H, m, CHSe); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 4.24 (q × 2), 23.90 (t), 32.65 (t × 2), 45.33 (d × 2). Anal. calcd for $C_7H_{14}Se_2$: C, 32.83; H, 5.51; found, C, 32.27; H, 5.38%.

trans-1,2-Bis(methylseleno)-1-methylcyclohexane (**2c**) (*0.11 g, 38%*). Results by IR (film), 2940, 2850, 1440, 1420, 1360, 1260, 1220, 1180, 1150, 1100, 1080, 1040, 960, 900, 820, 760, 700, 660 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$-TMS δ) 1.40–1.53 (1H, m, alkyl H), 1.56 (3H, s, Me), 1.62–1.63 (2H, m, alkyl H), 1.72–1.88 (1H, m, alkyl H), 1.96 (3H, s, SeMe), 2.04 (3H, s, SeMe), 2.19–2.22 (1H, m, alkyl H), 3.11–3.14 (1H, m, SeCH); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 2.28 (q), 5.78 (q), 22.97 (t), 25.17 (t), 25.99 (q), 30.98



SCHEME 2 i: 1 eq *n*-BuLi/MeI (71%), lithium 2,2,6,6-tetramethylpiperidide/MeI (96%), or 50% NaOH/MeI/Bu_4NHSO_4 (85%). ii: 4 eq NBS (67%).

(t), 38.46 (t), 48.39 (s), 52.47 (d); HRMS calcd for $C_9H_{18}Se_2$: 285.9699; found: 285.9719.

1-Methyl-1-methylselenocyclohexane (**3c**) (*0.05 g, 26%*). Results by IR (film), 3000–2850, 1440, 1370, 1250, 1140, 1080, 960, 900, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 1.25–1.31 (1H, m, alkyl H), 1.39–1.52 (4H, m, alkyl H), 1.44 (3H, s, Me), 1.61–1.66 (2H, m, alkyl H), 1.74–1.76 (2H, m, alkyl H), 1.87 (3H, s, SeMe); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 0.42 (q), 23.12 (t), 25.93 (t), 29.66 (q), 38.90 (t), 43.66 (s); HRMS calcd for $C_8H_{15}Se$: 192.0417; found: 192.0410.

threo-2,3-Bis(methylseleno)heptane (**2d**) (*0.28 g, quant.*). Results by IR (film), 3590, 2950, 2930, 900, 660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 0.91 (3H, t, J = 7 Hz, CH_2 Me), 1.31–1.39 (4H, m, alkyl H), 1.52 (3H, d, J = 7 Hz, CHMe), 1.65–1.69 (1H, m, alkyl H), 1.75–1.80 (1H, m, alkyl H), 2.02 (3H, s, SeMe), 2.04 (3H, s, SeMe), 2.92–2.93 (1H, m, CHSeMe), 3.13–3.16 (1H, m, CHSeMe); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 4.24 (q), 4.94 (q), 14.30 (q), 20.32 (q), 22.75 (t), 30.16 (t), 34.24 (t), 42.44 (d), 50.87 (d); HRMS calcd for $C_9H_{20}Se_2$: 287.9893; found: 287.9873.

erythro-2,3-Bis(methylseleno)heptane (**2e**) (*0.19 g, 66%*). Results by IR (film), 3600, 2920, 740, 660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 0.92 (3H, t, J = 7 Hz, CH_2Me), 1.30–1.41 (4H, m, alkyl H), 1.44 (3H, d, J = 7 Hz, CHMe), 1.56–1.59 (1H, m, alkyl H), 1.81–1.98 (1H, m, alkyl H), 2.00 (3H, s, SeMe), 2.01 (3H, s, SeMe), 2.92–2.97 (1H, m, CHSe), 3.27–3.29 (1H, m, CHSe); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 4.16 (q), 4.42 (q), 13.93 (q), 17.75 (q), 22.34 (t), 30.75 (t), 30.97 (t), 41.70 (d), 49.17 (d), Anal. calcd for $C_9H_{20}Se_2$: C, 37.77; H, 7.04; found: C, 37.59; H, 7.04%.

1,2-Bis(methylseleno)-1-trimethylsilylethane (**2f**) (*quant.*). Results by IR (film), 3600, 2975, 2940, 1420, 1250, 1200, 1120, 1010, 900, 860, 760, 680, 660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 0.06 (9H, s, Me_3Si), 1.95 (3H, s, MeSe), 2.01 (3H, s, MeSe), 2.03–2.05 (1H, m, 1-H), 2.84 (1H, dd, J = 9 and 12 Hz, 2-H), 3.03 (1H, dd, J = 6 and 12 Hz, 2-H); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) – 1.99 (q), 4.70 (q), 5.70 (q), 28.51 (d), 29.54 (t). Anal. calcd for $C_7H_{18}SeSi$: C, 29.17; H, 6.29; found: C, 28.15; H, 6.12%.

3,4-Bis(methylseleno)butan-1-ol (**2g**) (*0.09 g, 33%*). Results by IR (film), 3600–3100 (OH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 1.72–1.81 (1H, m, 2-H), 2.01 (3H, s, SeMe), 2.04 (3H, s, SeMe), 2.18–2.26 (1H, m, 2-H), 2.80–2.86 (1H, dd, J = 11 and 14 Hz, 3-H), 3.06–3.10 (2H, m, $SeCH_2$), 3.82–3.84 (2H, t, J = 6 Hz, CH_2O); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 2.59 (q), 5.07 (q), 32.62 (t), 36.60 (t), 37.77 (d), 61.24 (t). Anal. calcd for $C_6H_{14}OSe_2$: C, 27.71; H, 5.43; found: C, 27.53; H, 5.33%.

1,2-Diphenyl-1-methylselenoethane (**3h**) (*0.07 g, 26%*). Results by IR (film), 3500, 3250, 3100, 2925, 2850, 1940, 1860, 1800, 1600, 1490, 1450, 1420, 1270, 1180, 1140, 1020, 900, 760, 740, 700, 600 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 1.73 (3H, s, SeMe), 3.22–3.33 (2H, m, CH_2), 4.13–4.17 (1H, t, J = 8 Hz, CH), 7.10–7.27 (10H, m, ArH). Anal. calcd for $C_{15}H_{16}Se$: C, 65.45; H, 5.86; found, C, 65.72; H, 5.86%.

(E)- and (Z)-1,4-Bis(methylseleno)-2,3-dimethyl-2-butene (**2i**) (*0.15 g, 55%*) (*E:Z = 1:1*). Results by IR (film), 2925, 1420, 1370, 1260, 1180, 900, 660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 1.80 (s, Me), 1.81 (s, Me), 1.94 (s, SeMe), 3.30 (s, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 3.57 (q), 4.08 (q), 18.25 (q), 18.69 (q), 28.60 (t), 29.01 (t), 128.40 (s), 128.53 (s). Anal. calcd for $C_8H_{16}Se_2$: C, 35.57; H, 5.97; found: C, 35.40; H, 5.87%.

2,3-Dimethyl-1-methylseleno-2-butene (**3i**) (*0.03 g, 16%*). Results by IR (film), 2950–2980, 1460, 1370, 1280, 1180, 900 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 1.69 (6H, s, Me), 1.75 (3H, s, Me), 1.90 (3H, s, SeMe), 3.29 (2H, s, Se CH_2); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 3.31 (q), 18.07 (q), 20.61 (q), 20.86 (q), 28.97 (t), 124.40 (s), 124.94 (s); HRMS calcd for $C_7H_{14}Se$: 178.0246; found: 178.0253.

1,4-Bis(methylseleno)-2-methyl-2-butene (**2j**) (*0.08 g, 32%*) (*E:Z = 7:2*). Results by IR (film), 3600, 3200, 3000, 2950, 1830, 1640, 1430, 1380, 1280, 1200, 1120, 900, 740, 660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 1.78 (s, *E*- and *Z*-Me), 1.90 (s, *E*-SeMe), 1.95 (s, *Z*-SeMe), 1.96 (s, *E*-SeMe), 1.97 (s, *Z*-SeMe), 3.17–3.25 (m, allyl H), 5.43–5.47 (m, olefinic H); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 3.45 (*E*-q), 3.78 (*E*- and *Z*-q), 15.11 (*E*-q), 21.59 (*Z*-t), 21.99 (*E*-t), 22.78 (*Z*-q), 25.06 (*Z*-t), 34.17 (*E*-t), 123.73 (*E*-d), 123.85 (*Z*-d), 134.48 (*E*-s), 134.57 (*Z*-s); MS *m/z*: 163 (M^+ – SeMe).

(E)- and (Z)-1,4-Bis(methylseleno)-2,3-diphenyl-2-butene (**2k**) (*0.28 g, 72%*) (*E:Z = 92:8*). Colorless needles, mp 117–118°C. Results by IR (KBr), 3000, 2925, 1860, 1800, 1740, 1595, 1570, 1490, 1440, 1410, 1260, 1150, 1070, 1020, 940, 915, 860, 760, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 1.69 (s, *E*-Me), 1.93 (s, *Z*-Me), 3.37 (s, *E*-CH_2), 3.77 (s, *Z*-CH_2), 7.28–7.40 (m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 4.80 (*Z*-q), 4.90 (*E*-q), 28.35 (*Z*-t), 30.23 (*E*-t), 126.34 (d), 126.54 (d), 127.89 (d), 137.03 (*E*-s), 137.11 (*Z*-s), 140.95 (s), 141.43 (*Z*-s). Anal. calcd for $C_{18}H_{20}Se_2$: C, 54.83; H, 5.11; found: C, 54.63; H, 5.06.

(E)-2,3-Diphenyl-1-methylseleno-2-butene (**3k**) (*0.08 g, 28%*). Colorless prisms, mp 47–48°C. Re-

sults by IR (film), 3100–3000, 2970, 2850, 1600, 1570, 1490, 1440, 1280, 1190, 1160, 1100, 1030, 1000, 990, 920, 760, 700, 660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 1.67 (3H, s, SeMe), 1.87 (3H, s, Me), 3.42 (2H, s, CH_2), 7.25–7.40 (10H, m, ArH). Anal. calcd for $C_{17}H_{16}Se$: C, 67.78; H, 6.02; found: C, 67.48; H, 6.00%; MS, *m/z*, 302 (M^+), 207 (M^+ − SeMe).

4,5-Bis(methylseleno)-1-pentene (**2l**) (*0.25 g, 97%*). Results by IR (film), 3100, 2950, 2820, 1640, 1420, 1280, 1260, 1210, 1000, 910, 660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 2.02 (3H, s, SeMe), 2.03 (3H, s, SeMe), 2.39–2.47 (1H, m, alkyl H), 2.64–2.70 (1H, m, alkyl H), 2.79–2.86 (1H, m, alkyl H), 2.98–3.04 (2H, m, alkyl H), 5.11–5.16 (2H, m, olefinic H), 5.79–5.84 (1H, m, olefinic H); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 3.07 (q), 5.10 (q), 31.57 (t), 38.41 (t), 40.31 (d), 117.32 (t), 135.39 (d). Anal. calcd for $C_7H_{14}Se_2$: C, 32.81; H, 5.51; found: C, 33.01; H, 5.49%.

5,6-Bis(methylseleno)-1-hexene (**2m**) (*0.24 g, 88%*). Results by IR (film), 3100, 3000, 2900, 2850, 1720, 1640, 1280, 1140, 1000, 920, 660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 1.59–1.67 (1H, m, alkyl H), 1.98 (3H, s, SeMe), 2.01 (3H, s, SeMe), 2.16–2.31 (2H, m, alkyl H), 2.82 (1H, dd, J = 9 and 12 Hz, CH_2Se), 2.90–2.95 (1H, m, CHSe), 3.05 (1H, dd, J = 5 and 12 Hz, CH_2Se), 4.98–5.09 (2H, m, olefinic H), 5.78–5.86 (1H, m, olefinic H); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 2.80 (q), 5.37 (q), 32.07 (t), 32.80 (t), 33.53 (t), 40.97 (d), 115.41 (t), 138.03 (d). Anal. calcd for $C_8H_{16}Se_2$: C, 35.57; H, 5.97; found: C, 35.37; H, 5.89%.

N,N-Bis[2,3-bis(methylseleno)propyl]-p-toluenesulfonamide (**2n**) (*0.16 g, 50%*). Results by IR (film), 1490 (SO_2N), 1160 (SO_2N) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 2.03 (6H, s, SeMe × 2), 2.07 (3H, s, SeMe), 2.08 (3H, s, SeMe), 2.44 (3H, s, Me), 2.88–3.13 (4H, m, CH_2), 3.27 (4H, m, CH_2Se), 3.53–3.66 (2H, m, CHSe), 7.33 (2H, d, J = 8 Hz, ArH), 7.70 (2H, d, J = 8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 3.12 (q), 3.29 (q), 5.76 (q × 2), 21.42 (q), 29.42 (t), 40.10 (d), 50.71 (t), 54.91 (t), 127.44 (d), 127.55 (d), 129.65 (d), 134.77 (s), 135.25 (s), 143.62 (s), 143.68 (s). Anal. calcd for $C_{17}H_{29}Se_4$: C, 32.55; H, 4.66; N, 2.23; found: C, 32.74; H, 4.62; N, 2.24%.

N-Allyl-N-[2,3-bis(methylseleno)propyl]-p-toluenesulfonamide (**3n**) (*0.04 g, 20%*). Results by IR (film), 1500 (SO_2N), 1160 (SO_2N) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 2.01 (3H, s, SeMe), 2.07 (3H, s, SeMe), 2.44 (3H, s, Me), 2.90–3.00 (2H, m, NCH_2), 3.19 (1H, dd, J = 6 and 14 Hz, CH_2Se), 3.27–3.32 (1H, m, alkyl H), 3.57 (1H, dd, J = 8 and 14 Hz, CH_2Se), 5.13–5.19 (2H, m, olefinic H), 5.53–5.63 (1H, m, olefinic H), 7.31 (2H, d, J = 8 Hz, ArH), 7.72 (2H, d, J = 8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 5.14 (q), 5.59 (q), 21.53 (q), 29.18 (t), 40.21 (d), 51.91 (t), 52.29 (t), 119.67 (t), 127.38 (d), 129.76 (d), 132.83 (d), 136.20 (s), 143.52 (s).

trans-3,4-Bis(methylseleno)-1-cyclooctene (**2o**) (*0.16 g, 53%*). Results by IR (film), 3010, 2950, 2850, 1440, 1420, 1320, 1270, 1240, 1220, 1180, 1120, 1080, 1060, 990, 940, 900, 830, 780, 720, 660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 1.30–1.36 (1H, m, alkyl H), 1.59–1.79 (5H, m, alkyl H), 1.95 (3H, s, SeMe), 2.01 (3H, s, SeMe), 3.11–3.16 (1H, m, CHSe), 3.96–4.02 (1H, brt, J = 11 Hz, CHSe), 5.53–5.58 (1H, m, olefinic H), 5.75–5.81 (1H, m, olefinic H); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 3.92 (q), 4.73 (q), 23.53 (t), 27.02 (t), 28.37 (t), 31.15 (t), 40.92 (d), 46.97 (d), 131.65 (d), 132.83 (d). Anal. calcd for $C_{10}H_{18}Se_2$: C, 39.88; H, 5.99; found: C, 40.55; H, 6.13%.

4-Methylseleno-1-cyclooctene (**3o**) (*0.06 g, 30%*). Results by IR (film), 3050, 2940, 2850, 1450, 1280, 1260, 1240, 1160, 1080, 1000, 960, 900, 840, 780, 770, 720, 660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 1.25–1.43 (2H, m, alkyl H), 1.53–1.72 (3H, m, alkyl H), 1.91–1.94 (1H, m, alkyl H), 1.98 (3H, s, SeMe), 2.07–2.12 (1H, m, alkyl H), 2.17–2.23 (1H, m, alkyl H), 3.82–3.89 (1H, m, 1-H), 5.54–5.59 (1H, m, olefinic H), 5.64–5.71 (1H, m, olefinic H); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 3.07 (q), 26.26 (t), 26.37 (t), 26.70 (t), 29.37 (t), 35.90 (d), 36.16 (t), 130.54 (d), 133.58 (d). Anal. calcd for $C_9H_{16}Se$: C, 53.20; H, 7.94; found: C, 53.48; H, 7.95%.

Alkylation Reactions of (E)-1,4-Bis(methylseleno)-2,3-diphenyl-2-butene (**2k**). (a) *n*-BuLi (0.15 mL, 0.75 mmol) was added dropwise to a THF (1 mL) solution of **2k** (0.15 g, 0.5 mmol) at −78°C under an Ar atmosphere. After the reaction mixture had been stirred for 5 minutes, a THF (1 mL) solution of MeI (0.11 g, 0.75 mmol) was added dropwise to the mixture. The whole was warmed to room temperature and then was treated with sat. NH_4Cl solution and water (150 mL). The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel with hexane. 2,3-Diphenyl-1,3-butadiene (**1k**) (0.73 g, 71%) was obtained as colorless needles.

(b) A THF (1 mL) solution of **2k** (0.15 g, 0.5 mmol) was added dropwise to a THF (2 mL) solution of lithium 2,2,6,6-tetramethylpiperidide (1.3 mmol). The reaction mixture was treated by the same procedure as for (a). The compound **1k** (0.10 g, 96%) was obtained.

(c) A mixture of **2k** (0.15 g, 0.5 mmol) and MeI (0.71 g, 5 mmol) in ether (2 mL) was added to a mixture of tetrabutylammonium hydrosulfate (0.03 g, 0.1 mmol) in 50% NaOH solution (0.5 mL). The reaction mixture was stirred overnight and treated

in the same procedure as for (a). The compound **1k** (0.09 g, 85%) was obtained.

Reaction of **2k** *with N-Bromosuccinimide.* *N*-Bromosuccinimide (0.23 g, 1.3 mmol) was added to a dry CH_2Cl_2 (2 mL) solution of **2k** (0.10 g, 0.32 mmol) at 0°C. The reaction mixture was stirred for 1 hour and then the solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel with CH_2Cl_2-hexane (1:5). (*E*)- and (*Z*)-1,4-dibromo-2,3-diphenyl-2-butene (**5**) (0.08 g, 67%) (*E*:*Z* = 5:1) was obtained as colorless prisms, mp 148–151°C. Results by IR (KBr), 3060, 3030, 1960, 1570, 1500, 1440, 1330, 1260, 1220, 1150, 1070, 1020, 1000, 980, 930, 910, 780, 770, 710, 680 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-TMS δ) 4.05 (s, *E*-CH_2), 4.50 (s, *Z*-CH_2), 7.08–7.46 (m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$-TMS δ) 32.37 (*Z*-t), 35.70 (*E*-t), 127.43 (*Z*-d), 127.96 (*Z*-d), 128.18 (*E*-d), 128.33 (*E*-d), 128.46 (*Z*-d), 128.58 (*Z*-d), 129.19 (*Z*-d), 138.07 (*E*-s), 139.19 (*E*-s), 139.37 (*Z*-s), 139.89 (*Z*-s). Anal. calcd for $C_{16}H_{14}Br_2$: C, 52.49; H, 3.85; found: C, 52.53; H, 3.90%.

REFERENCES

[1] D. L. J. Clive, S. M. Menchen, *J. Org. Chem., 44*, 1979, 4279.

[2] A. Cravador, A. Krief, *Tetrahedron Lett., 22*, 1981, 2491; T. Kataoka, M. Yoshimatsu, H. Shimizu, Y. Kawase, M. Hori, *Heterocycles, 31*, 1990, 889.

[3] T. Kataoka, M. Yoshimatsu, H. Shimizu, M. Hori, *Tetrahedron Lett., 31*, 1990, 5927; T. Kataoka, M. Yoshimatsu, Y. Noda, T. Sato, H. Shimizu, M. Hori, *J. Chem. Soc., Perkin. Trans., 1*, 1993, 121.

[4] A. Ogawa, H. Tanaka, H. Yokoyama, R. Obayashi, K. Yokoyama, N. Sonoda, *J. Org. Chem., 57*, 1992, 111.

[5] B. Hermans, N. Colard, L. Hevesi, *Tetrahedron Lett., 33*, 1992, 4629.

[6] D. G. Garrat, G. H. Schmid, *Can. J. Chem.*, 1974, 3599.

[7] F. Toda, Y. Takehira, Y. Kataoka, K. Mori, T. Sato, M. Segawa, *J. Chem. Soc., Chem. Commun.*, 1984, 1234.

[8] D. Liotta, M. Saindane, D. Brothers, *J. Org. Chem., 47*, 1982, 1598.

[9] M. Sevrin, J. N. Denis, A. Krief, *Tetrahedron Lett., 21*, 1980, 1877.

[10] J. W. Anderson, G. K. Barker, J. E. Drake, M. Rodger, *J. Chem. Soc. Dalton Trans.*, 1973, 1716.