Synthesis of Functionalized Tetrahydrofurans by Electrophile-Induced Cyclization of 4-Alkenals

Norbert De Kimpe,* Mark Boelens, and Jan Baele

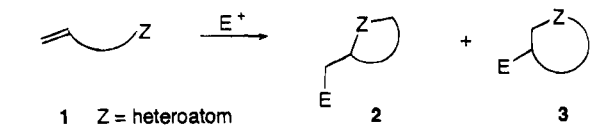
Department of Organic Chemistry, Faculty of Agricultural and Applied Biological Sciences, University of Gent, Coupure Links 653, B-9000 Gent, Belgium

Received March 10, 1994

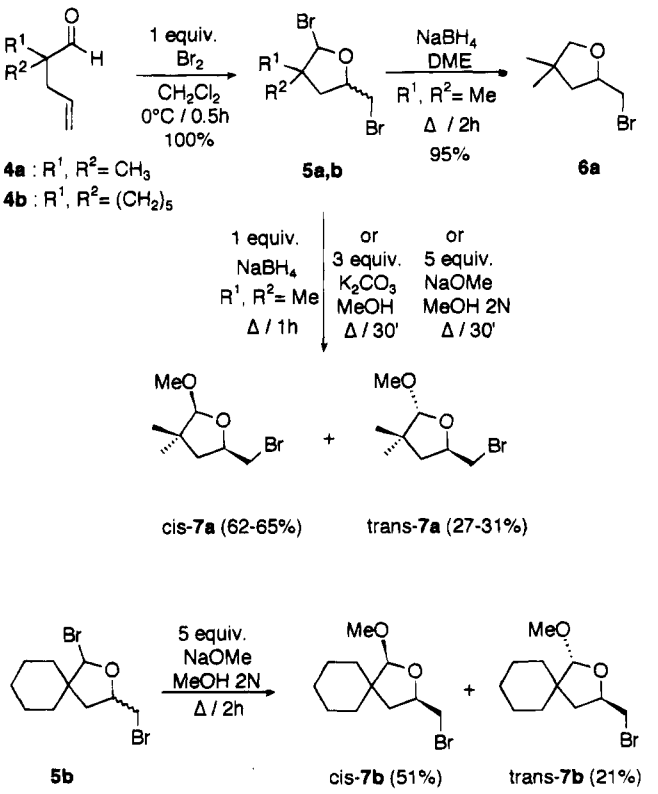
Electrophile-induced cyclizations of substrates **1**, carrying an olefinic double bond and a nucleophile Z, have become very popular in modern organic synthesis (Scheme 1).[1-3] Olefinic double bonds have been utilized in these cyclizations to generate the electrophilic site by addition of electrophiles to form an intermediate onium species (π-complex) that is intramolecularly captured by the nucleophilic part to give heterocycles **2** and/or **3**.[1-3] Internal nucleophiles that have been used include alcohols, carboxylic acids, secondary amines, thiols, imino-type nitrogens (e.g., imines, imidates, thioimidates, oximes, ...), carbamates, and carbamoyl functions.[1,2,4,5] Thus far, carbonyl oxygens have not been reported to participate in such reactions. However, in situ generated hydroxyl groups, as in the addition of alcohols to carbonyl compounds, can also react in phenylseleno–etherification processes, as exemplified by the formation of tetrahydropyrans from 4-alkenals[6] and 5-alkenones.[7] In this paper, the direct carbonyl participation of 4-alkenals in an intramolecular way under the influence of electrophilic activation of the olefinic double bond without added nucleophile is reported.

2,2-Disubstituted 4-pentenals **4** instantaneously react with 1 molar equiv of bromine in dichloromethane at 0 °C to afford the highly reactive 2-bromo-5-(bromomethyl)-tetrahydrofurans **5a** and **5b** in quantitative yield (Scheme 2). One stereoisomer was formed, but it proved to be difficult to determine its stereochemistry due to the unstable nature (fuming liquids) of dibromotetrahydrofurans **5a** and **5b**.[8] Reductive removal of the 2-bromo atom was easily accomplished with sodium borohydride in 1,2-dimethoxyethane, giving rise to 2-(bromomethyl)-4,4-dimethyltetrahydrofuran (**6a**) in 95% yield. An analogous reaction in methanol afforded the corresponding 2-methoxylated tetrahydrofurans **7a** as mixtures of cis- and trans-isomers (cis/trans 2/1; NOE measurements). Identical results for the synthesis of 2-methoxy tetrahydrofurans **7a** were obtained by treatment of **5a** with potassium carbonate in methanol under reflux or with an excess of sodium methoxide in methanol under reflux. In all experiments, nearly the same yields were obtained for *cis*-**7a** (62–65%) and *trans*-**7a** (27–31%). A similar reaction of the reactive spiro compound **5b** with excess sodium methoxide in methanol gave access to *cis*-3-(bromomethyl)-1-methoxy-2-oxabicyclo[4.5]decane (*cis*-**7b**) and *trans*-3-(bromomethyl)-1-methoxy-2-oxabicyclo-[4.5]decane (*trans*-**7b**) in 51% and 21% yield, respectively. It should be pointed out that the cis–trans ratio of tetrahydrofurans **7a** and **7b** does not reflect the stereochemistry in **5a** and **5b**. The first-order nucleophilic substitution of the bromo atom at the 2-position of **5** takes place via an intermediary oxonium ion. Finally, attack by methoxide at the 2-position leads to *cis*-**7** and *trans*-**7**.

Scheme 1



Scheme 2

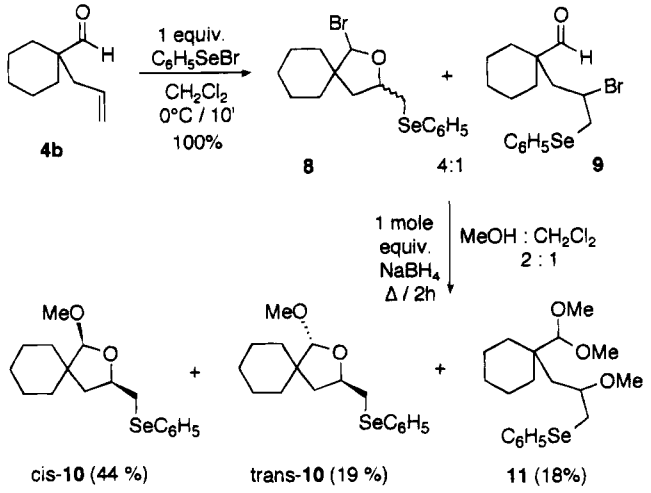


The electrophile-induced reaction of α-allylcyclohexanecarboxaldehyde **4b** with phenylselenenyl bromide was investigated next. Surprisingly, the addition of 1 equiv of phenylselenenyl bromide to the α-allyl aldehyde **4b** in dichloromethane at 0 °C affords a reaction mixture containing 2-bromo-5-[(phenylselenenyl)methyl]tetrahydrofuran **8** (*cis*-**8**:*trans*-**8** in a ratio of 1:2 or vice versa) as the major compound and the Markownikoff addition product **9** as a minor compound (ratio **8**:**9** 4:1) (Scheme 3). Successive treatment of this reaction mixture with 1 mol equiv of sodium borohydride in methanol under reflux afforded the corresponding 2-methoxylated tetrahydrofurans **10** (as a mixture of cis- and trans-isomers) and the acetal **11** (ratio **10**:**11** 71:29). Purification of the latter reaction mixture by flash chromatography gave the oxaspiro compounds *cis*- and *trans*-**10** as a mixture (*cis*-**10**:*trans*-**10** in a ratio of 7:3), in addition to the acetal **11**. Although NMR irradiation techniques and NOE

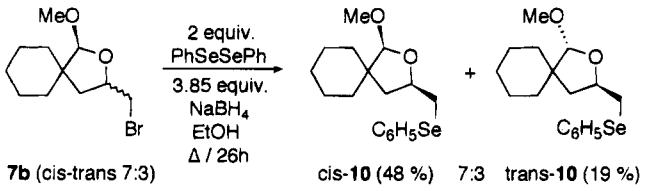
(1) Nicolaou, K. C.; Petasis, N. A.; Claremon, D. A. In *Organoselenium Chemistry*; Liotta, D., Ed.; Wiley-Interscience: New York, Chichester 1987, Chapter 2, pp 127–162 and references cited therein.
(2) Cardillo, G.; Orena, M. *Tetrahedron* **1990**, *46*, 3321–3408 and references cited therein.
(3) Paulmier, C. In *Selenium Reagents and Intermediates in Organic Synthesis*; Baldwin, J. E., Ed.; Pergamon Press: Oxford, 1986, Chapter 8, pp 229–255 and references cited therein.
(4) De Kimpe, N.; Boelens, M. *J. Chem. Soc., Chem. Commun.* **1993**, 916–918 and references cited therein.
(5) Harmange, J.-C.; Figadère, B. *Tetrahedron Asymmetry* **1993**, *4*, 1711–54.
(6) Current, S.; Sharpless, K. B. *Tetrahedron Lett.* **1978**, 5075–5078.
(7) Ley, S. V.; Lygo, B. *Tetrahedron Lett.* **1982**, *23*, 4625–28.
(8) ^{1}H NMR NOE experiments failed to reach definitive conclusions about the stereochemistry of tetrahydrofurans **5a** and **5b**.

0022-3263/94/1959-5485$04.50/0

Scheme 3



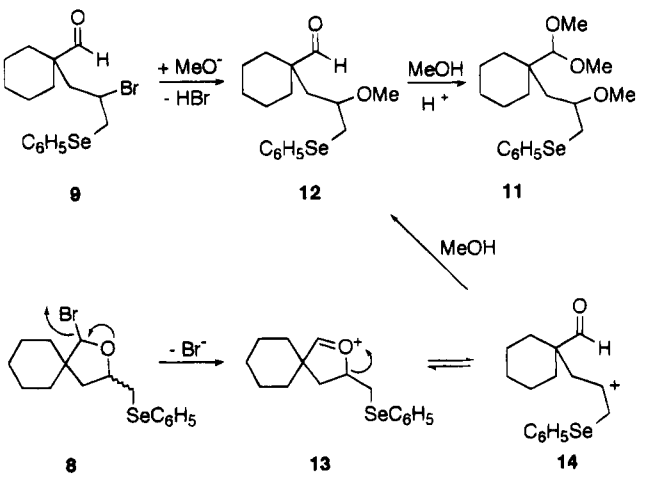
Scheme 4



measurements were carried out on the mixture *cis*-**10** and *trans*-**10**, it was impossible to determine the stereochemistry of both isomers. To solve this stereochemical problem, attempts at the transformation of bromide **7b** (cis–trans ratio 7:3) to the selenide **10** were made (Scheme 4). After reaction of **7b** with phenylselenium anion (1.23 equiv) in ethanol for 28 h under reflux only 40% conversion of the starting material was measured. The reaction mixture contained *cis*-**7b**, *cis*-**10**, and *trans*-**10** in a ratio of 6:2:2 (measured by ^{1}H NMR). The trans-isomer *trans*-**7b** reacted apparently faster than the cis-isomer *cis*-**7b** to afford the corresponding *trans*- and *cis*-**10**. As expected, no exchange of the methoxy unit by ethoxy had taken place, indicative of retention of configuration. Treatment of **7b** (cis–trans ratio 7:3) with an excess of sodium phenylselenolate (4 equiv, 26 h reflux) in ethanol gave a complete conversion of **7b** to **10** (cis:trans ratio 7:3). These results, in combination with the known stereochemistry of *cis*-**7b** and *trans*-**7b**, led to the stereochemical determination of *cis*-**10** and *trans*-**10**. The mechanism for the formation of the acetal **11**, which was isolated in a pure state by flash chromatography, can be interpreted as nucleophilic substitution of **9** to the methoxylated seleno compound **12**, which is converted to the acetal **11** (Scheme 5). In an alternative route, 2-bromotetrahydrofuran **8** can eliminate the bromide anion to the oxonium ion **13**, which is in equilibrium with the carbenium ion **14**. The latter can react further with methanol to the methoxylated aldehyde **12**, which is converted to the acetal **11**. As such, it is not clear whether the acetal **11** is originating from the spiro compound **8** or the γ-bromo aldehyde **9**.

It seems that the present cyclofunctionalization is limited to nontautomerizable alkenals. Not unexpectedly, tautomerizable aldehydes also suffer attack by electrophiles at the enol function, giving rise to mixtures of reaction products. 2-Methyl-4-pentenal (**4**) (R^1 = Me; R^2 = H) did not afford tetrahydrofurans upon treatment

Scheme 5



with bromine in dichloromethane. Quite surprisingly, temporarily blocking the α-position of 4-alkenals by α-chlorination did not provide a solution to the problem, as exemplified by the failure to isolate any reaction product from the reaction of 2-chloro-2-methyl-4-pentenal (**4**) (R^1 = Me; R^2 = Cl) with bromine.

In conclusion, a useful electrophile-induced cyclization of 4-alkenals to afford functionalized tetrahydrofurans via direct carbonyl participation under the influence of electrophilic activation is reported. Research work is in progress to determine the scope and limitations of the cyclofunctionalization, which is promising for the synthesis of heterocyclic spiro compounds.

Experimental Section

General Methods.[9,10] All solvents were dried by conventional methods. Ether and dichloromethane were distilled over sodium and calcium hydride, respectively. TLC: Merck Kieselgel 60 F 254, precoated. Column chromatography: Merck Kieselgel 60, 0.04–0.063 mm (flash).

Synthesis of 4-alkenals 4 proceeded by condensation of the appropriate allylic alcohol and the corresponding aldehyde in a Claissen rearrangement type reaction, with azeotropic distillation of the water formed, as described in the literature.[11,12]

Synthesis of 2-Bromo-5-(bromomethyl)tetrahydrofurans 5. In a 250-mL flask 2,2-dimethyl-4-pentenal (**4a**) (5.60 g, 50 mmol) was dissolved in dry dichloromethane (50 mL) and cooled in an ice bath. Bromine (7.99 g, 50 mmol), dissolved in dry dichloromethane (20 mL), was added dropwise to the cooled mixture. After the mixture was stirred for 0.5 h at 0 °C, the solvent was evaporated *in vacuo* and 2-bromo-5-(bromomethyl)-3,3-dimethyltetrahydrofuran (**5a**) was obtained as a pale yellow liquid (13.58 g, 100%). The crude product was highly moisture sensitive and was immediately used in further reactions. IR (NaCl, film): ν_{max} = 2960, 1062, 990 (broad), 664 cm^{-1}. ^{1}H NMR (CCl_4; 60 MHz) δ: 1.20 and 1.30 (each 3H, each s), 1.6–2.4 (2H, m), 3.3–3.8 (2H, m), 4.3–4.9 (1H, m), 6.30 (1H, s). MS (70 eV) *m/z*: 270/2/4 (no M^+), 191/3 (7), 132 (2), 115 (3), 83 (11), 81 (7), 69 (8), 67 (5), 55 (30), 53 (6), 43 (100), 41 (51). Anal. Calcd for $C_7H_{12}Br_2O$: C, 30.91; H, 4.45. Found: C, 30.71; H, 4.58. Due to the instability of **5a** ^{13}C NMR-data were not obtained.

1-Bromo-3-(bromomethyl)-2-oxabicyclo[4.5]undecane (5b) was prepared from α-allyl-cyclohexanecarboxaldehyde (**4b**) by the same procedure as for **5a**. **5b** was obtained quantitatively as a liquid. IR (NaCl, film): ν_{max} = 2925, 2850, 1452, 1067 cm^{-1}. ^{1}H NMR (CCl_4; 60 MHz) δ: 1.2–2.3 (12H, m), 3.2–4.9 (3H, m),

(9) Enders, D.; Tiebes, J.; De Kimpe, N.; Keppens, M.; Stevens, C.; Smagghe, G.; Betz, O. *J. Org. Chem.* **1993**, *58*, 4881–4884.
(10) Boeykens, M.; De Kimpe, N. *Synthesis* **1992**, 1109–1112.
(11) Salomon, G.; Ghosh, S. *Organic Syntheses*; Wiley: New York, 1990; Collect. Vol. 7, p 177.
(12) Brannock, K. C. *J. Am. Chem. Soc.* **1959**, *81*, 3379–83.

6.52 (1H, s). MS (70 eV) *m/z*: 310/2/4 (no M^+), 231/3 (12), 202/4 (2), 155 (13), 123 (93), 95 (6), 93 (6), 91 (6), 81 (100), 79 (14), 69 (10), 67 (48), 55 (21), 49 (9), 45 (9), 44 (14), 43 (13), 41 (55). Due to the instability of **5b** ^{13}C NMR-data were not obtained.

Synthesis of 2-(Bromomethyl)-4,4-dimethyltetrahydrofuran (6a). To a solution of 2-bromo-5-(bromomethyl)-3,3-dimethyltetrahydrofuran **(5a)** (2.72 g, 0.01 mol) in dimethoxyethane (25 mL) was added sodium borohydride (0.76 g, 0.02 mol) portionwise, and the mixture was stirred for 2 h at reflux temperature. The mixture was cooled, poured into H_2O (100 mL), extracted with dichloromethane (3 × 50 mL), and dried ($MgSO_4$). After filtration, the solvent was removed *in vacuo* affording 1.83 g (95%) of 2-(bromomethyl)-3,3-dimethyltetrahydrofuran **(6a)**. A pure analytical sample was prepared by preparative GC. IR (NaCl, film): ν_{max} = 2950, 2860, 1368, 1051 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz): δ 1.11 and 1.12 (each 3H, each s), 1.54 (1H, d × d, J = 8.9, 12.4 Hz), 1.90 (1H, d × d, J = 12.4, 6.2 Hz), 3.41 (1H, d × d, J = 9.8, 5.6 Hz), 3.47 (1H, d × d, J = 9.8, 5.6 Hz), 3.54 (1H, d, J = 8.0 Hz), 3.58 (1H, d, J = 8.0 Hz), 4.24–4.34 (1H, m). ^{13}C NMR ($CDCl_3$, 68 MHz): δ 25.93, 26.43, 36.28, 40.20, 45.37, 78.34, 80.57. MS (70 eV) *m/z*: 192/4 (no M^+), 100 (11), 99 (100), 83 (5), 81 (25), 79 (4), 71 (5), 69 (9), 67 (5), 57 (5), 56 (5), 55 (49), 53 (6), 43 (65), 42 (7), 41 (37). Anal. Calcd for $C_7H_{13}OBr$: C, 43.54; H, 6.79. Found: C, 43.62; H, 6.69.

Synthesis of 2-(Bromomethyl)-4,4-dimethyl-5-methoxytetrahydrofuran (7a). To a solution of 2-bromo-5-(bromomethyl)-3,3-dimethyltetrahydrofuran **(5a)** (1.36 g, 0.005 mol) in absolute methanol (20 mL) was added sodium borohydride (0.19 g, 0.005 mol), and the reaction mixture was stirred for 1 h at reflux temperature. The reaction mixture was poured into H_2O (60 mL) and extracted with dichloromethane (3 × 30 mL). The organic layers were combined and dried ($MgSO_4$). After filtration, the solvent was removed *in vacuo*, and 1.03 g of **7a** was obtained (92%). Identical results were obtained when **5a** was treated with 3 equiv of potassium carbonate in methanol under reflux (30 min) or with 5 equiv of sodium methoxide in methanol (2 N) under reflux (30 min). For each experiment, the crude liquid reaction product contained *cis*-**7a** and *trans*-**7a** in a ratio of 7:3. Both isomers could only be separated by capillary gas chromatography. A pure analytical sample of the cis- and trans-mixture was prepared by preparative GC. IR (NaCl, film): ν_{max} = 2920, 1180, 1098, 1030, 970 cm^{-1}.

Spectrometrical data of *cis*-**7a** in the mixture. ^1H NMR ($CDCl_3$, 270 MHz) δ: 1.04 and 1.07 (each 3H, each s), 1.65 (1H, d × d, J = 12.2, 8.6 Hz), 1.89 (1H, d × d, J = 12.2, 6.9 Hz), 3.29 (1H, d × d, J = 9.8, 7.3 Hz), 3.34 (3H, s), 3.47 (1H, d × d, J = 9.8, 6.3 Hz), 4.31–4.43 (1H, m), 4.41 (1H, s); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 21.71, 25.84, 37.14, 43.73, 44.24, 54.59, 78.60, 111.01. MS (70 eV) *m/z*: 222/4 (no M^+), 191/3 (14), 130 (5), 129 (60), 97 (13), 87 (16), 85 (16), 83 (100), 82 (14), 81 (4), 79 (4), 69 (45), 67 (13), 55 (75), 43 (55), 41 (53).

Spectrometrical data of *trans*-**7a** in the mixture. ^1H NMR ($CDCl_3$, 270 MHz) δ: 1.06 and 1.09 (each 3H, each s), 1.56 (1H, d × d, J = 12.7, 6.3 Hz), 2.00 (1H, d × d, J = 12.7, 8.2 Hz), 3.37 (3H, s), 3.39–3.51 (2H, m), 4.31–4.34 (1H, m), 4.51 (1H, s). ^{13}C NMR ($CDCl_3$, 68 MHz) δ: 22.23, 27.94, 35.85, 48.98, 44.24, 55.25, 76.64, 111.62. MS (70 eV) *m/z*: 222/4 (no M^+), 191/3 (8), 129 (24), 97 (6), 87 (8), 85 (22), 84 (7), 83 (100), 82 (12), 69 (30), 67 (11), 55 (67), 43 (38), 41 (39).

Synthesis of 3-(Bromomethyl)-1-methoxy-2-oxabicyclo-[4.5]decane (7b). A solution of 1-bromo-3-(bromomethyl)-2-oxabicyclo[4.5]decane (**5b**) (0.62 g, 2 mmol) and sodium methoxide in methanol (5 mL, 2 N) was stirred for 2 h at reflux temperature. The reaction mixture was then poured into H_2O (20 mL) and extracted with dichloromethane (3 × 15 mL). The organic layers were combined and dried ($MgSO_4$). After filtration, the solvent was removed *in vacuo*, and a mixture of *cis*- and *trans*-**7b** was obtained (cis/trans = 71/29). Both isomers could not be separated. A pure analytical sample of the isomeric mixture was prepared by preparative GC. IR (NaCl, film): ν_{max} = 2930, 1101, 1030, 991 cm^{-1}.

Spectral data for *cis*-**7b** in the mixture. ^1H NMR ($CDCl_3$, 270 MHz) δ: 1.3–1.6 (11H, m), 2.05 (1H, d × d, J = 7.1, 12.4 Hz), 3.29 (1H, d × d, J = 7.2, 9.6 Hz); 3.35 (3H, s), 3.47 (1H, d × d, J = 6.3, 9.6 Hz), 4.2–4.4 (1H, m), 4.58 (1H, s). ^{13}C NMR ($CDCl_3$, 68 MHz) δ 22.64, 22.98, 26.06, 31.68, 33.80, 37.39, 40.25, 48.34, 54.68, 78.06, 109.50. MS (70 eV) *m/z*: 310/2 (no M^+), 231/3 (12), 169 (21), 123 (73), 95 (13), 81 (100), 79 (17), 69 (17), 67 (60), 55 (25), 44 (15), 41 (43).

Spectral data for *trans*-**7b** in the mixture. ^1H NMR ($CDCl_3$, 270 MHz) δ: 1.3–1.6 (11H, m), 1.93 (1H, d × d, J = 8.6, 12.8 Hz), 3.36 (3H, s), 3.3–3.5 (2H, m), 4.2–4.4 (1H, m), 4.63 (1H, s). ^{13}C NMR ($CDCl_3$, 68 MHz) δ: 22.98, 23.77, 25.84, 31.71, 33.80, 36.05, 36.37, 47.10, 54.97, 76.13, 110.22. MS (70 eV) *m/z*: 310/2 (no M^+), 231/3 (12), 169 (21), 123 (73), 95 (13), 81 (100), 79 (17), 69 (17), 67 (60), 55 (25), 44 (15), 41 (43).

Synthesis of 1-Methoxy-3-[(phenylselenenyl)methyl]-2-oxaspiro[4.5]decane (10). Method A. To a cooled (0 °C) solution of α-allylcyclohexanecarboxaldehyde **(4b)** (0.61 g, 4 mmol) in dry dichloromethane (10 mL) was added portionwise phenylselenenyl bromide. After the solution was stirred at 0 °C for 10 min, absolute methanol (20 mL) and sodium borohydride (0.15 g, 4 mmol) were added successively. The solution was stirred for 2 h under reflux and then cooled to room temperature, poured into H_2O (100 mL), and extracted with dichloromethane (3 × 50 mL). After drying ($MgSO_4$) and filtration, the solvent was evaporated *in vacuo*. The crude reaction mixture was purified by flash chromatography (silica gel, ethyl acetate:hexane (5:95) as eluent) affording 0.86 g of *cis*- and *trans*-**10** (R_f = 0.20, 63%, ratio of *cis*-**10**:*trans*-**10** 70:30) and 0.27 g of 1-[2-methoxy-3-(phenylselenenyl)propyl]cyclohexane-1-carboxaldehyde dimethyl acetal (**11**) (R_f = 0.10, 18%). The cis- and trans-isomers **10** could not be separated.

Method B. To an ethanolic solution of sodium phenylselenolate, prepared by addition of sodium borohydride (0.29 g, 7.7 mmol) to diphenyl diselenide (1.25 g, 4 mmol) in absolute ethanol (33 mL),[13] was added dropwise at room temperature the freshly prepared cis–trans mixture (ratio 7:3) of **7b** (0.53 g, 2 mmol), dissolved in absolute ethanol (5 mL). The reaction mixture was stirred for 26 h at reflux temperature. The reaction was quenched by pouring the mixture into a hydrochloric acid solution (100 mL, 0.2 N). After extraction with dichloromethane (3 × 25 mL), the organic layers were combined and dried ($MgSO_4$). Evaporation of the solvent *in vacuo* afforded a crude yellow oil which, after flash chromatography (silica gel, ethyl acetate:hexane (5:95) as eluent), gave the oxaspiro compound **10** in pure state (0.45 g, 67%, R_f = 0.20) as a mixture of *cis*-**10** and *trans*-**10** (ratio of *cis*-**10**:*trans*-**10** 72:28). IR (NaCl, film): ν_{max} = 2950, 1098, 1030, 1023, 988, 748. ^1H NMR (270 MHz, $CDCl_3$) δ: 1.16–1.78 (2 × 11H, m), 4.24–4.35 (2 × 1H, m), 7.22–7.25 (2 × 3H, m), 7.50–7.53 (2 × 2H, m); specific signals for the minor isomer are δ 1.92 (1H, d × d, J = 12.6, 8.56 Hz), 2.99 (1H, d × d, J = 11.9, 6.93 Hz), 3.14 (1H, d × d, J = 11.9, 6.27 Hz), 3.33 (3H, s), 4.59 (1H, s); specific signals for the major isomer are δ 2.02 (1H, d × d, J = 12.3, 6.76 Hz), 2.93 (1H, d × d, J = 11.9, 7.26 Hz), 3.20 (1H, d × d, J = 11.9, 6.27 Hz), 3.32 (3H, s), 4.53 (1H, s); ^{13}C NMR ($CDCl_3$, 68 MHz): major isomer, δ 22.64, 23.63, 26.09, 31.73, 33.69, 35.45, 36.57, 48.28, 54.54, 77.75, 109.31, 126.75, 129.00, 130.13, 132.50; minor isomer, δ 23.00, 23.79, 25.75, 31.66, 36.57, 25.89, 33.84, 47.19, 54.75, 75.83, 109.31, 126.88, 129.00, 132.68, 132.57. Due to the instability of the isomeric compounds *cis*-**10** and *trans*-**10**, it was impossible to obtain the mass spectral data by the GC–MS technique.

Spectral data of the acetal **11**. IR (NaCl, film): ν_{max} = 2924, 1090, 1074, 740 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ: 1.25–1.47 (10H, m), 1.73 (2H, d, J = 5.28 Hz), 3.03 (1H, d × d, J = 11.9, 6.60 Hz), 3.11 (1H, d × d, J = 11.9, 4.62 Hz), 3.28 (3H, s), 3.45 and 3.47 (each 3H, each s), 3.62–3.67 (1H, m), 4.07 (1H, s), 7.22–7.25 (3H, m), 7.51–7.52 (2H, m). ^{13}C NMR ($CDCl_3$, 68 MHz) δ: 21.40, 21.51, 26.27, 30.06, 31.46, 33.30, 36.96, 41.40, 55.99, 68.56, 77.88, 112.51, 126.65, 128.93, 130.99, 132.57. MS (70 eV, direct inlet) *m/z*: 386 (M^+, 8), 215 (25), 184 (42), 165 (6), 158 (6), 151 (8), 125 (7), 91 (7), 81 (8), 75 (100), 47 (8), 41 (7); only the peaks for the most abundant isotope ^{80}Se are reported. Anal. Calcd for $C_{19}H_{30}O_3Se$: C, 59.21; H, 7.85. Found: C, 59.35; H, 7.69.

Acknowledgment. We are indebted to the Belgian "National Fund for Scientific Research" and the "Instituut voor de Bevordering van het Wetenschappelijk Onderzoek in Nijverheid en Landbouw" for financial support of this research.

(13) Grieco, D. A.; Miyashita, M. *Tetrahedron Lett.* **1974**, 1869–1871.