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One-Step Introduction of Two Substituents onto 7-Oxabicyclo[2.2.1]hept-5-en-2-one Derivatives *via* Radical Phenylselanyl-Group Transfer Reactions

Philippe Renaud* and **Jean-Paul Vionnet**

Abstract. Radical-mediated phenylselanyl-group transfer reactions have been used to introduce simultaneously substituents at the C(6)-*endo*- and C(5)-*exo*-positions of 7-oxabicyclo[2.2.1]hept-5-en-2-one derivatives. The key steps are a radical addition to a silyl ketene acetal and the cyclization of a 1-alkoxy-substituted ester radical.

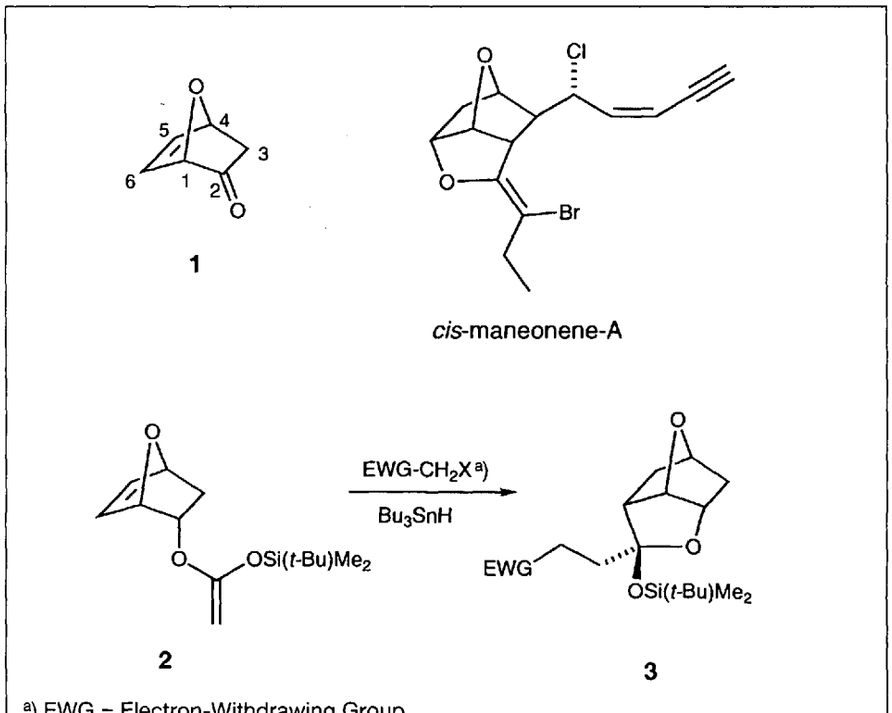
Both enantiomers of 7-oxabicyclo-[2.2.1]hept-5-en-2-one ((±)-**1**) ('naked sugars') are easily prepared from furan [1] and are suitable precursors for polysubstituted 7-oxanorbornan-2-ones. Previous work by *Vogel* and coworkers has shown that the latter are readily converted into a large variety of biologically relevant compounds [2]. This method is mostly limited to 7-oxanorbornan-2-one derivatives substituted at C(5) and C(6) by hydroxy and amino groups. The stereoselective introduction of carbon residues at C(5) and C(6) is highly desirable as it would open new routes for the preparation of C-glycosides, branched carbohydrates and natural products. In a recent series of papers, we have reported that direct [3][4] and indirect [5] radical additions to **1** and derivatives of **1** allow regio- and stereoselective introduction of carbon moieties. The indirect method using a radical addition to silyl ketene acetal **2** followed by a very fast 5-*exo-trig* cyclization is efficient for the formation of an *endo* C–C bond at C(6) (see *e.g.* **3**, *Scheme 1*) [5]. Introduction of substituents at C(5) and C(6) in a one step procedure is highly desired for synthetic purposes. Indeed, several natural products isolated from Hawaian marine alga *Laurencia nidifica*, such as *cis*-maneonene-A, possess such a substitution pattern [6]. In this communication we report our attempts to introduce in a one-step procedure one *endo*-substituent at C(6) and one *exo*-substituent at C(5) using radical cascade procedures.

In a first experiment starting from (±)-**2**, (phenylthio)acetonitrile, and allylstannane gave (±)-**4** which was produced *via* a 1,5-H shift of (±)-**5** leading to (±)-**6** (EWG = CN) (*Scheme 2*). It was possible to avoid the H shift by running the reaction with chloromethyl phenyl sulfone (EWG = SO_2Ph). In that case, the absence of H shift may be explained by the radical destabilizing effect of the sulfonyl group [7]. Compound (±)-**7** was isolated in a modest 38% yield after optimization of the reaction conditions.

We decided to turn our attention to a procedure using a radical phenylselanyl group transfer reaction with the dimethyl (phenylselanyl)propanedioate (±)-**8** as radical precursor [8] Recently, we have demonstrated that this type of reactions is particularly useful when subsequent rearrangement of the radical intermediate has to be favored [3] because of the slowness of the phenylselanyl transfer reaction [9]. The use of the electrophilic malonyl radical should ensure a selective and fast addition to the silyl ketene acetal (±)-**2**. Indeed, irradiation with a 300 W sunlamp of a solution of (±)-**8** and (±)-**2** in benzene for 12 h gave the expected product (±)-**9** in 75% yield (*Scheme 3*).

The efficiency of the phenylselanyl transfer was further demonstrated by the cyclization of the α-alkoxy-α-phenylselanyl ester (±)-**12**. This compound was easily prepared from the alcohol (±)-**10** by

Scheme 1



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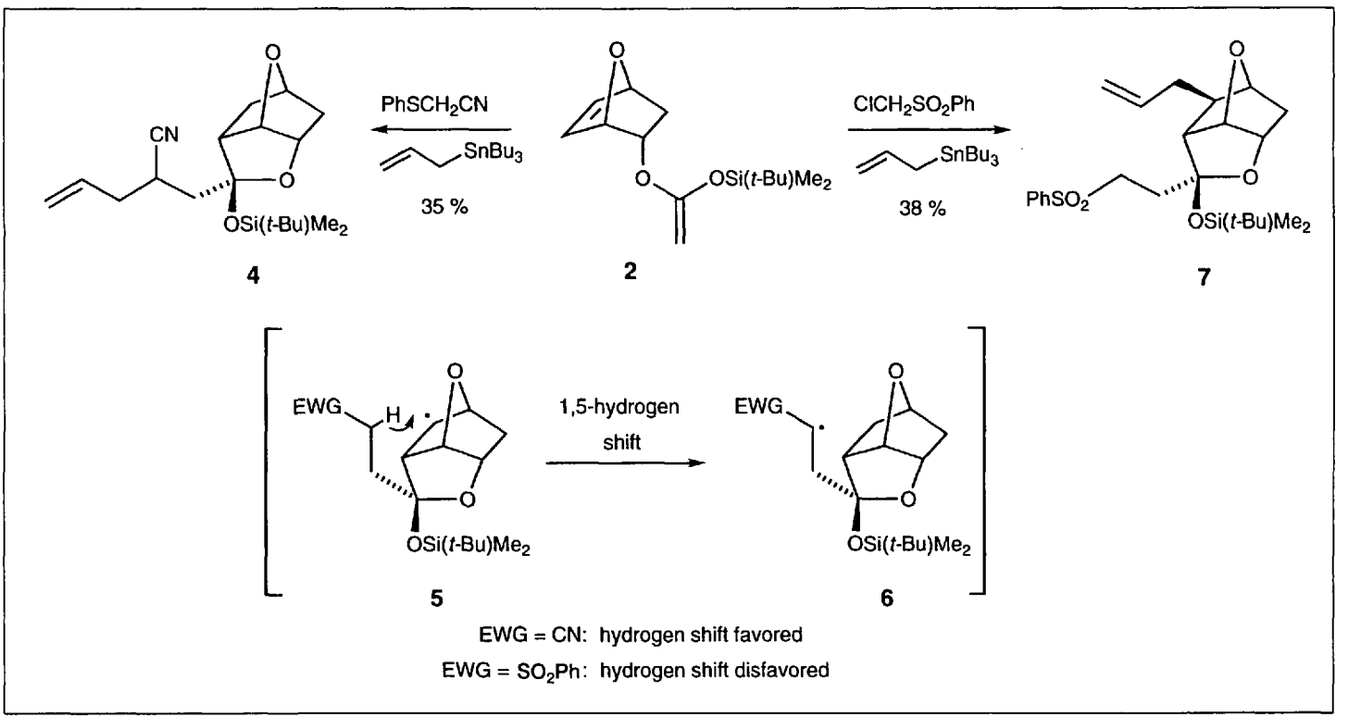
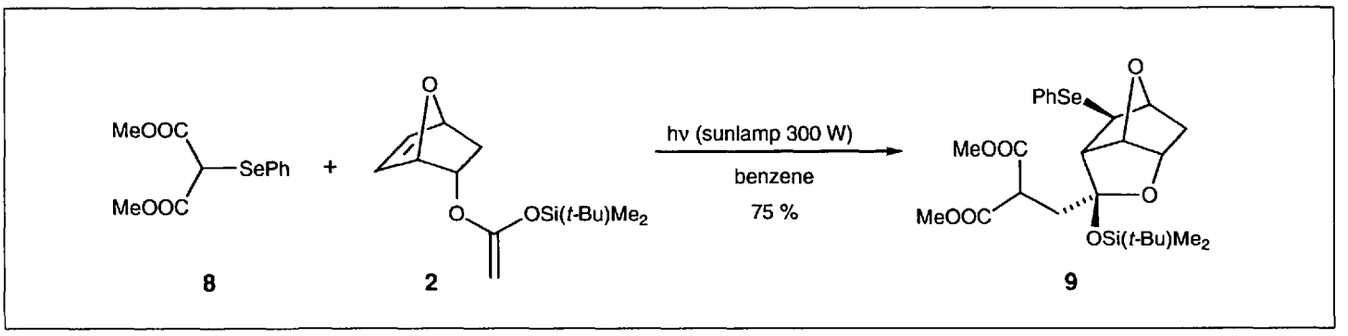
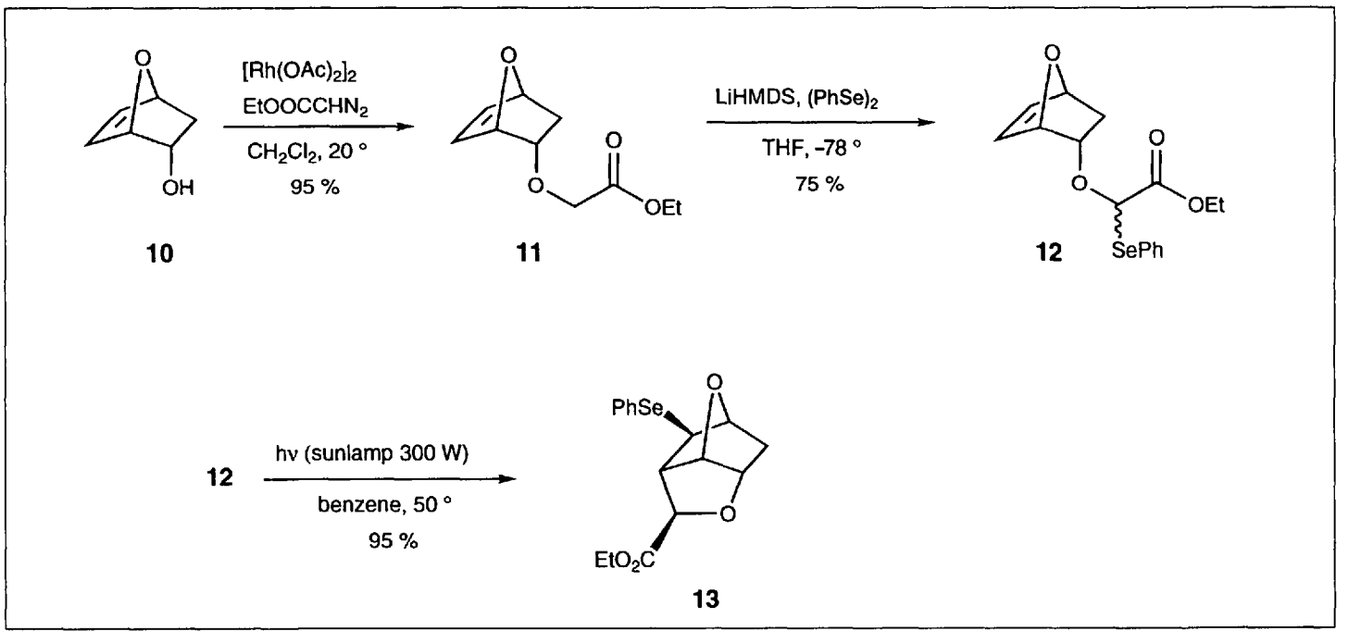
Scheme 2



Scheme 3



Scheme 4



treatment with ethyl diazoacetate in the presence of $[Rh(OAc)_2]_2$ [10]. The obtained ester (±)-**11** was then selanylated under standard conditions (LiHMDS, $(PhSe)_2$. Irradiation of (±)-**12** with a 300 W sunlamp produced the tricyclic compound (±)-**13** in 95% yield. Interestingly, this reaction was fast and all the starting material was consumed in 3 h.

In conclusion, we have demonstrated that phenylselanyl group transfer reactions are highly efficient for the addition of radicals to nucleophilic alkenes such as silyl ketene acetal and for cyclization reactions of α-alkoxy ester radicals. The conservation of the synthetically versatile phenylselanyl group in the molecule offers numerous possibilities for further functionalization of the resulting products. By using this strategy, we have been able to introduce in one step and good yields, two substituents at C(6)-*endo*- and C(5)-*exo*-positions of a 7-oxanorbornen-2-one derivative.

Experimental Part

General. THF was freshly distilled from K under N_2. CH_2Cl_2 was distilled from P_2O_5. Benzene was distilled from CaH_2 under N_2. For flash column chromatography (FC) and filtration, *Merck* silica gel *60* (70-230 mesh) was used with ethyl acetate (AcOEt) and petroleum ether (PE) as solvents for elution. TLC were run on *Merck* silica gel *60* F_{254} anal. plates; detection either with UV, iodine or by spraying with a soln. of 25 g phosphomolybdic acid, 10 g of $Ce(SO_4)_2 \cdot 4\ H_2O$, 60 ml of conc. H_2SO_4 and 940 ml of H_2O with subsequent heating. M. p. (not corrected) were determined by using a *Büchi Totoli* apparatus. Bulb-to-bulb distillations were carried out using a *Büchi GKR-50* apparatus; b.p. refer to air bath temperature. The following apparatus were used: NMR: *Bruker AC-250 FT* (^{1}H/250 MHz, ^{13}C/62.9 MHz). Unless otherwise indicated, spectra were recorded in $CDCl_3$ and chemical shifts are given in ppm with TMS signal at 0.00 ppm. IR: *Perkin-Elmer 297* spectrophotometer. MS: *Finnigan 1020* and *Nermag R10-10C* (EI: electronic ionization 70 eV). Elemental analysis: *Ilse Beetz*, Mikroanalytisches Laboratorium, D-96317 Kronach. Irradiations were conducted using a sunlamp *Osram Ultra-Vitalux 300 W.*

*1-{[(*tert*-Butyl)dimethylsilyl]oxy}-1-{(1*RS,*2*RS,*4*RS*)-(7-oxabicyclo[2.2.1]hept-5-en-2-yl)oxy}ethene* ((±)-**2**) [5]. $NaBH_4$ (4.0 g, 100 mmol) was added to a cooled (–10°) soln. of (±)-**1** (11.0 g, 100 mmol) in MeOH (100 ml). The reaction mixture was stirred for 15 min, then warmed to r.t. and concentrated. A mixture of AcOEt (200 ml) and sat. NaCl soln. (100 ml) was added. After separation, the org. layer was dried ($MgSO_4$). Evaporation of the solvent and FC (AcOEt/PE 1:2) of the crude product gave the *endo*-alcohol (±)-**10** (10.0 g, 90%). A soln. of this alcohol (3.0 g, 30 mmol) in Ac_2O (30 ml) was treated with pyridine (7.0 ml, 88 mmol) and the reaction mixture was stirred at r.t. for 4 h then poured into a mixture of AcOEt (200 ml) and a 1M HCl soln. (100 ml). The org. layer was washed with sat. $NaHCO_3$ soln. (50 ml), brine (50 ml) and dried ($MgSO_4$). Evaporation of the solvent and bulb-to-bulb distillation of the crude product gave the acetate of (±)-**10** (3.9 g, 86%) as colorless oil. B.p. 100°/12 Torr. ^{1}H-NMR: 6.55 (*dd*, *J* = 5.8, 1.8, H–C(5)); 6.25 (*dd*, *J* = 5.8, 1.2, H–C(6)); 5.10 (*m*, H–C(1), H–C(2)); 4.95 (*dd*, *J* = 4.5, 1.8, H–C(4)); 2.39–2.23 (*m*, H_{exo}–C(3)); 1.95 (*s*, CH_3); 1.11 (*dd*, *J* = 2.0, *J* = 12.0, H_{endo}–C(3)). A 1M soln. of LDA (13 ml, 13 mmol) soln. in THF (20 ml) was cooled to –78° and a soln. containing the acetate of (±)-**10** (1.0 g, 6.5 mmol) and TBDMSCl (1.95 g, 13 mmol) in dry THF (10 ml) was added followed by HMPA (3 ml). The mixture was allowed to warm to r.t. over 4 h, poured into pentane (100 ml) washed with H_2O (3 x 50 ml), brine (2 x 50 ml) and dried ($MgSO_4$). Evaporation of the solvent and bulb to bulb distillation of the crude product gave (±)-**2** (1.6 g, 90 %) as colorless oil. B.p. 120°/0.01 Torr. ^{1}H-NMR: 6.52 (*dd*, *J* = 6.0, 1.8, H–C(5)); 6.30 (*dd*, *J* = 6.0, 1.8, H–C(6)); 5.05 (*ddd*, *J* = 4.5, 1.8, 0.7, H–C(1)); 4.95 (*ddd*, *J* = 5.0, 1.8, 0.7, H–C(4)); 4.54 (*ddd*, *J* = 7.5, 4.5, 2.5, H–C(2)); 3.28, 3.15 (2*d*, *J* = 2.5, H_2C=C), 2.25 (*ddd*, *J* = 7.5, 5.0, *J* = 12.0, H_{exo}–C(3)); 1.15 (*dd*, *J* = 12.0, 2.5, H_{endo}–C(3)); 0.9 (*s*, *t*-BuSi); 0.13, 0.12 (2*s*, Me_2Si). ^{13}C-NMR: 160.19 (*s*); 137.29 (*d*); 132.31 (*d*); 79.17 (*d*); 77.70 (*d*), 73.47 (*d*); 62.35 (*t*); 33.06 (*t*); 25.45 (*q*); 17.96 (*s*); –4.62 (*q*). Anal. calc. for $C_{14}H_{24}O_3Si$ (268.43): C 62.64, H 9.01; Si 10.46; found: C 62.61, H 9.02, Si 10.39.

*(2*RS,*2*SR*)-2-{{(1*RS,*3*SR,*5*SR,*6*RS,*7*SR*)-5-[[(*tert*-Butyl)dimethylsilyl]oxy]-4,8-dioxatricyclo[4.2.1.0^{3,7}]non-5-yl]methyl}pent-4-enenitrile* ((±)-**4**). A soln. of (±)-**2** (1.0 g, 3.7 mmol), phenylthioacetonitrile (1.6 g, 11.2 mmol), allyltributylstannane (5.0 g, 15 mmol) and AIBN (50 mg) in benzene (10 ml) was refluxed under N_2 for 12 h. AIBN (10 mg) was added every 4 h. Evaporation of the solvent and FC (AcOEt/PE 1:4) of the crude product gave (±)-**4** (455 mg, 35%) as colorless oil. IR (film): 3020*w*, 3000*w*, 2960*s*, 1640*w*, 1470*m*, 1250*s*, 1015*s*, 920*s*. EI-MS: 350 (1.81, $[M+1]^+$), 349 (0.45, M^+), 293 (22), 292 (98), 274 (44), 191 (34), 129 (48), 79 (100), 73 (99). ^{1}H-NMR: 5.90-5.58 (*m*, HC=C); 5.26–5.12 (*m*, H–C(7), H_2C=C); 4.52 (*t*, *J* = 4.9, H–C(1)); 4.35 (*dd*, *J* = 7.0, 4.9, H–C(3)); 2.93–2.78 (*ddt*, *J* = 11.0, 7.0, 3.0, CHCN); 2.65 (*ddd*, *J* = 11.0, 4.9, 2.3, H–C(6)); 2.5–2.25 (*m*, CH_2CH=C); 2.12–1.95 (*m*, H_{exo}–C(9), *CH*HCHCN); 1.90 (*dd*, *J* = 3.0, *J* = 14.5, CH*H*CHCN); 1.72–1.65 (*m*, H_{exo}–C(2)); 1.53 (*dd*, *J* = 2.5, *J* = 13.0, H_{endo}–C(9)); 1.46 (*d*, *J* = 13.0, H_{endo}–C(2)); 0.87 (*s*, *t*-BuSi); 0.11, 0.08 (2*s*, Me_2Si). ^{13}C-NMR: 132.63 (*d*); 121.34 (*s*); 119.48 (*t*); 107.11 (*s*); 83.76 (*d*); 77.64 (*d*); 76.17 (*d*); 48.74 (*d*); 41.53 (*t*); 40.68 (*t*); 37.38 (*t*); 33.76 (*t*); 27.15 (*d*); 25.71 (*q*); 17.8 (*s*); –3.16 (*q*); –3.74 (*q*). Anal. calc. for $C_{19}H_{31}O_3SiN$ (349.55): C 65.29, H 8.94; found: C 65.22, H 8.95.

*(1*RS,*3*RS,*5*RS,*6*SR,*7*RS,*9*SR*)-9-Allyl-5-[[(*tert*-butyl)dimethylsilyl]oxy]-5-[2-(benzenesulfonyl)ethyl]-4,8-dioxatricyclo[4.2.1.0^{3,7}]-nonane* ((±)-**7**). A soln. of (±)-**2** (804 mg, 3 mmol), allyltributylstannane (2.0 g, 6 mmol), chloromethyl phenyl sulfone (686 mg, 3.6 mmol) and AIBN (20 mg) in benzene (10 ml) was heated under reflux for 12 h. AIBN (10 mg) was added every 4 h. Evaporation of the solvent and FC (AcOEt/PE 1:5) of the crude product gave (±)-**7** (540 mg, 40%) containing 3–5% of an unidentified impurity. Colorless oil. ^{1}H-NMR: 7.88–7.95 (*m*, 2 arom. H); 7.55–7.75 (*m*, 3 arom. H); 5.85–5.60 (*m*, HC=C); 5.16–5.05 (*m*, H–C(7), C=CH_2); 4.35 (*dd*, *J* = 7.5, 4.5, H–C(3)); 4.22 (*d*, *J* = 4.5, H–C(1)); 3.22 (*dd*, *J* = 2.0, *J* = 8.5, *CH*HSO_2); 3.18 (*dd*, *J* = 1.5, *J* = 8.5, CH*H*SO_2); 2.30–1.90 (*m*, CH_2–CH=C, $CH_2CH_2SO_2$); 1.92 (*dd*, *J* = 5.0, 2.0, H–C(6)); 1.78–1.59 (*m*, H_{endo}–C(9), H_{exo}–C(2)); 1.42 (*d*, *J* = 12.0, H_{endo}–C(2)); 0.81 (*s*, *t*-BuSi); 0.35, 0.15 (2*s*, Me_2Si). ^{13}C-NMR: 138.06 (*s*); 136.62 (*d*); 133.81 (*d*); 129.31 (*d*); 128.07 (*d*); 117.11 (*t*); 107.08 (*t*); 83.32 (*d*); 80.00 (*d*); 77.86 (*d*); 55.29 (*d*); 54.60 (*d*); 52.61 (*t*); 44.18 (*d*); 40.57 (*t*); 38.42 (*d*); 32.10 (*t*); 26.79 (*d*); 25.62 (*q*); 17.72 (*s*); –3.83 (*q*).

*Dimethyl 2-{{(1*RS,*3*RS,*5*RS,*6*SR,*7*RS,*9*SR*)-9-(Phenylselanyl)-5-[[(*tert*-butyl)dimethylsilyl]oxy]-4,8-dioxatricyclo[4.2.1.0^{3,7}]non-5-yl]methyl}propanedioate* ((±)-**9**). A soln. of (±)-**2** (268 mg, 1.0 mmol) and dimethyl (phenylselanyl)propanedioate (400 mg, 1.4 mmol) in benzene (5 ml) was irradiated at 10° with a 300 W sunlamp under N_2 for 18 h. Evaporation of the solvent and FC (AcOEt/PE 1:10) of the crude mixture gave (±)-**9** (415 mg, 75%) as colorless oil. IR (film): 2940*s*, 2880*m*, 1740*s*, 1730*s*, 1580*m*, 1475*m*, 1300*s*, 900*m*. EI-MS: 554 (1.76, $[M+1]^+$), 553 (0.66, M^+), 525 (5), 499 (26), 467 (22), 341 (100), 113 (19), 75 (39), 73 (57). ^{1}H-NMR: 7.66 (*m*, 2 arom. H); 7.30 (*m*, 3 arom. H); 5.21 (*dd*, *J* = 5.0, 4.5, H–C(7)); 4.38 (*dd*, *J* = 7.0, 4.5, H–C(3)); 4.32 (*d*, *J* = 5.0, H–C(1)); 3.78, 3.72 (2*s*, 2 COOMe); 3.71 (*m*, *CH*(COOMe)$_2$); 3.30 (*d*, *J* = 2, H–C(9)); 2.58, 2.43 (*AB* part of an *ABX* system, J_{AB} = 15.0, $J_{AX} = J_{BX}$ = 6.0, CH_2CH(COOMe)$_2$); 2.28 (*dd*, *J* = 5.0, 2.0, H–C(6)); 1.57 (*ddd*, *J* = 7.0, 5.0, *J* = 14.0, H_{exo}–C(2)); 1.43 (*d*, *J* = 14.0, H_{endo}–C(2)); 0.85 (*s*, *t*-BuSi); 0.12, 0.08 (2*s*, Me_2Si). ^{13}C-NMR: 169.73 (*s*); 169.59 (*s*); 134.35 (*d*); 129.54 (*s*); 129.16 (*d*); 127.84 (*d*); 107.40 (*s*); 83.29 (*d*); 80.49 (*d*); 77.38 (*d*); 56.40 (*d*); 52.59 (*q*); 53.07 (*q*); 47.79 (*d*); 45.21 (*d*); 40.60 (*t*); 37.56 (*t*); 25.69 (*q*); 17.72 (*s*); –3.32 (*q*). Anal. calc. for $C_{25}H_{34}O_7SiSe$ (553.59): C 54.24, H 6.19, Si 5.07; found: C 54.27, H 6.29, Si 5.11.

*Ethyl [(1*RS,*2*RS,*4*RS*)-(7-Oxabicyclo-[2.2.1]hept-5-en-2-yl)oxy]acetate* ((±)-**11**). The *endo*-alcohol (±)-**10** was prepared from (±)-**1** as above in preparation of (±)-**2**. To a blue soln. of (±)-**10** (3.5 g, 3.15 mmol) and $[Rh(OAc)_2]_2$ (20 mg) in dry CH_2Cl_2 (15 ml) was added under N_2 a soln. of ethyl diazoacetate (3.6 g, 3.15 mmol) in CH_2Cl_2 (15 ml) over 4 h at r.t. Evaporation of the solvent and FC (AcOEt/PE 1:4) of the crude mixture gave unreacted (±)-**10** (2.0, 1.7 mmol) and (±)-**11** (2.56 g, 95%). Colorless oil. IR (film): 2980*s*, 1750*s*, 1440*m*, 1350*m*, 1275*m*, 1030*s*, 820*m*, 720*m*. EI-MS: 198 (0.2, M^+), 130 (6), 107 (5), 95 (10), 81 (29), 79 (19), 68 (100), 67 (34), 65 (26), 57 (60), 55 (18), 53 (21), 51 (10). ^{1}H-NMR: 6.55 (*dd*, *J* = 5.5, 1.8, H–C(5)); 6.38 (*dd*, *J* = 5.5, 1.5, H–C(6)); 5.0 (*dd*, *J* = 4.5, 1.5, H–C(1)); 4.93 (*dd*, *J* = 5.0, 1.8, H–C(4)); 4.21 (*q*, *J* = 7.0, OCH_2CH_3); 4.20 (*dd*, *J* = 8.0, 4.5, 2.2, H–C(2)); 4.13, 4.03 (*AB* spectra, J_{AB} = 16.0, OCH_2COOEt); 2.21 (*ddd*, *J* = 8.0, 5.0, *J* = 12.0, H_{exo}–C(3)); 1.39 (*t*, OCH_2CH_3); 1.16 (*dd*, *J* = 2.2, *J* = 12.0, H_{endo}–

C(3)). ^{13}C-NMR: 170.16 (*s*); 137.28 (*d*); 132.24 (*d*); 79.31 (*d*); 78.14 (*d*); 77.94 (*d*); 67.91 (*t*); 60.94 (*t*); 33.15 (*t*); 14.13 (*q*). Anal. calc. for $C_{10}H_{14}O_4$ (198.22): C 60.59, H 7.12; found: C 60.56, H 7.05.

*Ethyl (*RS*)-[(1*RS*,2*RS*,4*RS*)-(7-Oxabicyclo[2.2.1]hept-5-en-2-yl)oxy](phenylselanyl)acetate* ((±)-**12**). To a cooled (–78°) soln. of (±)-**11** (2.0 g, 10.1 mmol) in THF (30 ml) was added under N_2 a 0.7M LiHMDS soln. in THF (28.9 ml, 20.2 mmol). The mixture was stirred for 5 min and a soln. of diphenyldiselenide (3.15 g, 10.1 mmol) in THF (10 ml) was added. The mixture was allowed to warm to r.t. over 4 h and poured into a mixture of Et_2O (100 ml) and a 1M NH_4Cl soln. (50 ml). The org. layer was washed with brine (50 ml) and dried ($MgSO_4$). Evaporation of the solvent and FC (AcOEt/PE 1:4) of the crude mixture gave (±)-**12** (2.6 g, 73%) as a 1:1 mixture of isomers. EI-MS: 354 (0.99, $[M+1]^+$), 243 (10), 197 (7), 157 (16), 129 (9), 111 (9), 95 (38), 91 (11), 77 (52), 67 (100), 55 (27), 51 (26). ^{1}H-NMR: 7.68–7.56 (*m*, 2 arom. H); 7.40–7.22 (*m*, 3 arom. H); 6.50 (*dd*, *J* = 6.0, 2.0, H–C(5)); 6.30 (*dd*, *J* = 6.0, 1.8, H–C(6)); 5.41 (*s*, C*H*-COOEt); 5.02 (*dd*, *J* = 5.0, 2.0 H–C(4)); 4.53 (*ddd*, *J* = 8.0, 4.5, 2.5, H–C(2)); 4.13 (*q*, *J* = 6.5, OCH_2CH_3); 2.09 (*ddd*, *J* = 8.0, 5.0, *J* = 12.0, H_{exo}–C(3)); 1.21 (*t*, *J* = 6.5, OCH_2CH_3); 1.07 (*dd*, *J* = 2.5, *J* = 12.0, H_{endo}–C(3)). Anal. calc. for $C_{16}H_{18}O_4Se$ (353.27): C 54.40, H 5.14; found: C 54.36, H 5.21.

*(1*RS*,3*RS*,5*SR*,6*SR*,7*RS*,9*SR*)-5-(Ethoxycarbonyl)-9-(phenylselanyl)-4,8-dioxatricyclo[4.2.1.0^{3,7}]nonane* ((±)-**13**). A soln. of (±)-**12** (610 mg, 1.8 mmol) in degassed benzene (5 ml) was irradiated under N_2 at 50° with a 300 W sunlamp for 3 h. Evaporation of the solvent and FC (AcOEt/PE 1:4) of the crude mixture gave (±)-**13** (580 mg, 95%) as colorless oil. IR (film): 2980*s*, 2940*s*, 1740*s*, 1580*m*, 1480*m*, 1260*s*, 1200*s*, 1160*m*, 1080*s*, 1040*s*, 1020*s*, 980*m*, 890*m*, 750*s*. EI-MS: 354 (26 $[M+1]^+$), 353 (2, M^+), 281 (6), 197 (7), 171 (9), 123 (13), 105 (4), 99 (6), 95 (55), 81 (60), 77 (51), 67 (100), 55 (47). ^{1}H-NMR: 7.59–7.49 (*m*, 2 arom. H); 7.32–7.21 (*m*, 3 arom. H); 5.11 (*t*, *J* = 5.0, H–C(7)); 4.58 (*dd*, *J* = 7.0, 5.0, H–C(3)); 4.41 (*d*, *J* = 5.0, H–C(1)); 4.40 (*s*, H–C(5)); 4.13 (*q*, *J* = 7.0, OCH_2CH_3); 3.31 (*d*, *J* = 2.0, H–C(5)); 2.63 (*dd*, *J* = 5.0, 2.0, H–C(6)); 1.88 (*ddd*, *J* = 7.5, 5.0, *J* = 12.5, H_{exo}–C(2)); 1.53 (*d*, *J* = 12.5, H_{endo}–C(2)); 1.22 (*t*, *J* = 7.0, OCH_2CH_3). ^{13}C-NMR: 171.51 (*s*); 133.72 (*d*); 129.14 (*d*); 127.61 8 (*d*); 81.80 (*d*); 79.99 (*d*); 79.38 (*d*); 77.72 (*d*); 61.12 (*t*); 51.27 (*d*); 49.85 (*d*); 40.72 (*t*); 13.93 (*q*); one aromatic C(*d*) is 'missing'. Anal. calc. for $C_{16}H_{18}O_4Se$ (353.27): C 54.40, H 5.14, Se 22.35; found: C 54.30, H 5.12, Se 22.32.

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Korrekturen und Nachträge/ Corrections and Additions

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Rolf Steiger, 'Surface Chemistry of Silver Halide Microcrystals':
Fig. 5 has to be added.

Fig. 5. *Imaging SIMS iodide picture of AgBr microcrystals containing 0.13 mol-% iodide.* An iodide ring is predominantly formed along edges and corners of the cubic AgBr crystals (1.24-μm edge-length).