15. Reductive Radical Cyclisations of Bromo Acetals and (Bromomethyl)silyl Ethers of Terpenoid Alcohols

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The tin hydride promoted and the reductive vitamin B_{12} catalysed radical cyclisation of mixed 2-bromoacetaldehyde acetals and of (2-bromomethyl)dimethylsilyl ethers of allylic terpenoid alcohols has been investigated: 3-oxadeca-5,9-dien-1-yl radicals undergo 5-'*exo*' cyclisation to oxolanes (*Scheme 4*), 3-oxa-2-siladeca-5,9-dien-1-yl radicals sequential 6-'*endo*'→5-'*exo*' tandem cyclisation to *cis*-3-oxa-4-silabicyclo[4.3.0]nonanes (*Scheme 5*), and 3-oxa-2-silatetradeca-5,9,13-trien-1-yl radicals sequential 6-'*endo*'→6-'*endo*'→5-'*exo*' triple cyclisation to *trans-transoid-trans*-12-oxa-11-silatricyclo[7.4.0.$0^{2,6}$]tridecanes (*Scheme 6*).

Introduction. – It has become increasingly evident that sequential free-radical cyclisations of systems containing multiple olefinic bonds provide an attractive route to polycyclic compounds [1]. Very recently this has been exemplified by sequential cyclisations of functionalised alkenes, based on oxidative free-radical generation from β-keto esters with Mn^{III} and $Cu(OAc)_2$ [2] as well as based on acyl-radical generation from phenyl selenoesters with Bu_4SnH [3].

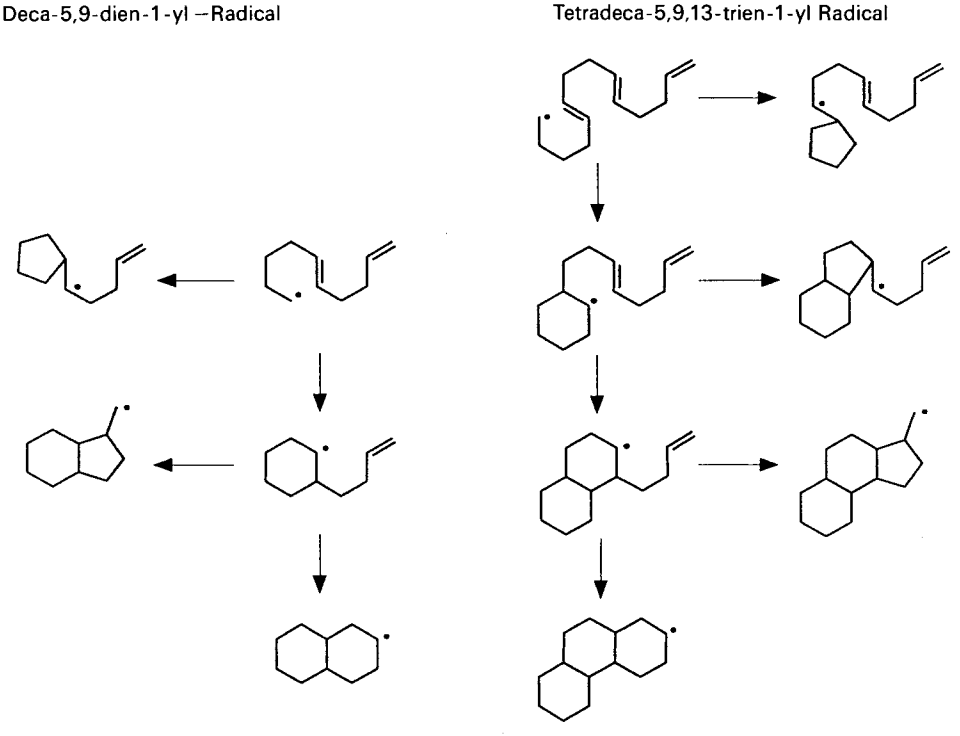
Early investigations by *Breslow et al.* were directed to the study of a potential free-radical mechanism in the oxidative cyclisation of squalene [4]. In this context, it has been found that the addition of benzoyloxy radicals to (*E*,*E*)-farnesyl acetate in presence of copper(II) benzoate gave selectively a *trans*-decalin derivative as the only bicyclic reaction product [5]. It should be noticed that the regio- and stereochemistry of cyclisations by oxidative radical processes may depend on the rate by which intermediate radicals are oxidised and subsequent steps occur along a cationic rather than a radical pathway [5] [6].

The factors influencing C,C-bond formation by 'clean' radical reactions are well understood [1]. The regioselectivity of hex-5-en-1-yl radical cyclisation is also well documented; with a few exceptions 5-'*exo*' cyclisation is generally preferred over 6-'*endo*' closure [7]. The factors determining the outcome of sequential radical cyclisation, however, require further investigation; the nature of the olefinic bonds that act as acceptors in succeeding cyclisations may influence the outcome of the preceding step, hence the possibility of a concerted pathway in free-radical multiple cyclisations has at least to be considered [8]. To this end, studies on the cyclisation of linear polyen-1-yl radicals bearing two or more olefinic bonds at all positions $4n + 1$ with $n > 0$ (as *e.g.* 5,9 and 5,9,13 *etc.*) are advised. Such polyen-1-yl radicals might undergo sequences of consecu-

[1]) Postdoctoral fellow under the auspices of the Royal Society.

[2]) Part of the planned Ph.D. thesis of *I. L.*, University of Bern.

Scheme 1. *Potential Pathways of Polyen-1-yl Radical Cyclisations.* Vertical arrows: 6-'*endo*' closures, horizontal arrows: 5-'*exo*' closures.

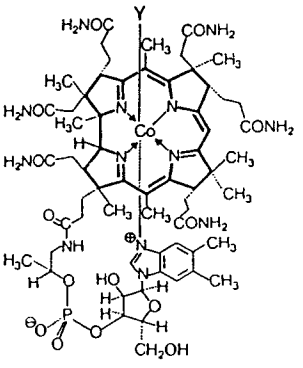


tive cyclisations as long as each step is preceded by a 6-'*endo*' ring closure. Each 5-'*exo*' step will break the sequence (if radical rearrangements are excluded). *Scheme 1* illustrates the formal cyclisation sequences of the two shortest members of such linear polyen-1-yl radicals (included are all 5-'*exo*' and 6-'*endo*' pathways, excluded are the disfavoured 5-'*endo*', 4-'*exo*' and medium-ring closures).

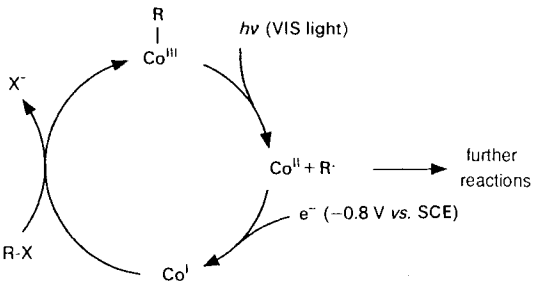
This study reports on reductive radical cyclisations of α-bromo acetals and (bromomethyl)silyl ethers of primary terpenoid alcohols, representing precursors of heteroatom analogues of the radicals shown in *Scheme 1*. The two types of alcohol derivatives were selected, since the potential corresponding C-centered radicals are expected to behave distinctly differently as initiators of the cyclisation sequences. Radicals obtained by abstraction of a Br-atom from α-bromo acetals undergo preferential 5-'*exo*' attack [9], whereas radicals derived from (bromomethyl)silyl ethers are reported to undergo both 5-'*exo*' and 6-'*endo*' cyclisation [10].

Radical species were generated by the well known Bu_3SnH method [11] or by the vitamin-B_{12}(Cbl)-catalysed, light-assisted electrochemical reduction [12]. The mechanism of the Cbl-catalysed radical generation is outlined in *Scheme 2*. Cob(I)alamin (obtained from Cob(III)alamin in two consecutive one-electron reductions) displaces X of RX with formation of an organocob(III)alamin and X^-. Photochemically induced Co,C-bond homolysis by irradiation with visible light (λ = 400–600 nm) affords the transient radical

Scheme 2. *Generation of C-Centered Radicals by Vitamin B_{12}-Photo-Electro-Catalysis*



Y = OH · HCl
Hydroxocobalamine hydrochloride
(vitamin B_{12a})



R· and the persistent radical cob(II)alamin. Its reduction to the catalytically active Cob(I)alamin occurs at potentials more negative than *ca.* –0.8 (*vs.* SCE).

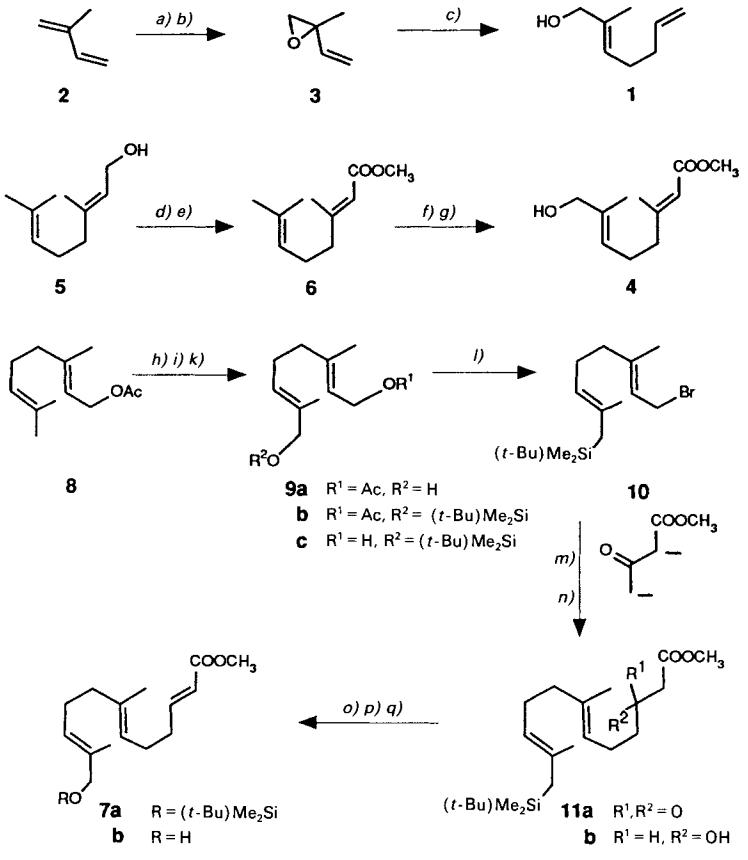
Results and Discussion. – *Bromo Acetals and (Bromomethyl)silyl Ethers of Terpenoid Alcohols.* The terpenoid allylic alcohols were synthesised as shown in *Scheme 3*.

(*E*)-Heptadienol **1** is accessible from isoprene (**2**) *via* epoxide **3** [13] in two steps by known procedures [14]. (2*E*,6*E*)-Methyl 8-hydroxy-3,7-dimethylocta-2,6-dienoate (**4**) was prepared from geraniol (**5**) *via* the known ester **6** [15] which was submitted to allylic oxidation with SeO_2 followed by $NaBH_4$ reduction [16]. (2*E*,6*E*,10*E*)-Methyl 12-hydroxy-7,11-dimethyldodeca-2,6,10-trienoate (**7b**) was obtained from geranyl acetate (**8**) *via* **9**–**11** in 8 steps (*ca.* 6% overall yield): allylic oxidation with SeO_2 followed by $NaBH_4$ reduction [16], protection of the alcohol as a (*t*-Bu)Me_2Si ether, solvolysis of the AcO function and conversion of the alcohol to the bromide by the *Corey-Kim-Takeda* procedure [17], chain extension with the dianion of methyl acetoacetate according to *Büchi* and *Wüst* [18], reduction of the carbonyl function using $NaBH_4$, elimination of H_2O *via* tosylation, and removal of the silyl protecting group. The structure assignment of **7b** is based on spectroscopic data confirming the (2*E*)-configuration (^{1}H-NMR: $J(2,3) = 16.5$ Hz).

The racemic 2-bromoacetaldehyde acetals **12** and **13** (see below, *Scheme 4*) were made from the alcohols **1** and **4**, respectively, with *N*-bromosuccinimide (NBS) and ethyl vinyl ether in CH_2Cl_2 by a known procedure [19]. The (bromomethyl)silyl ethers **14**–**16** (see below, *Schemes 5* and *6*) were prepared from the alcohols **1**, **4**, and **7b**, respectively, by treatment with (bromomethyl)chlorodimethylsilane in CH_2Cl_2 in the presence of Et_3N and catalytic amounts of 4-(dimethylamino)pyridine ($Me_2NC_5H_4N$) [10].

Radical Cyclisation Procedures. For radical cyclisation by the tin-hydride method [11], the starting bromo derivative was dissolved in benzene, and a solution containing Bu_3SnH (*ca.* 30–50% excess with respect to substrate) and catalytic amounts of 2,2′-azobis[isobutyronitrile] (= 2,2′-dimethyl-2,2′-azobis[propanenitrile]; AIBN) in benzene was slowly added by a mechanical syringe pump to the boiling (*ca.* 80°) solution. Products were isolated by chromatography and their structure determined by spectroscopic methods.

Scheme 3. *Synthesis of the Allylic Alcohols* **1**, **4**, *and* **7b**

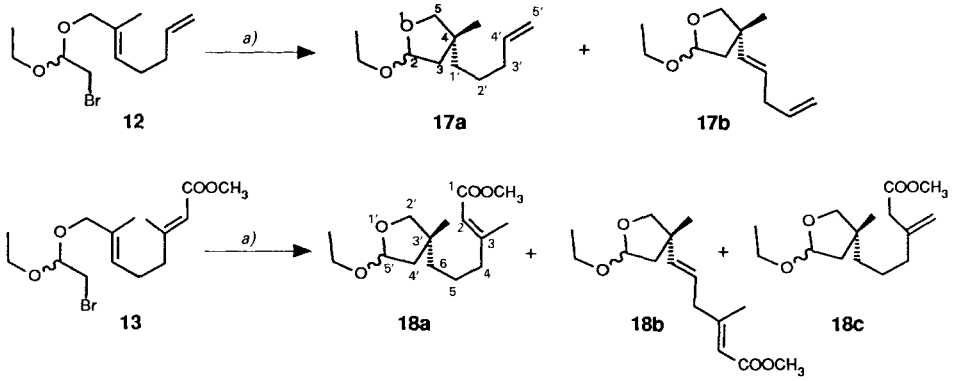


a) NBS, H_2O, 18–25°. *b*) 30% NaOH soln., 10–15°. *c*) Allyl chloride, Mg/I_2, CuI, THF, –25°. *d*) MnO_2, hexane, 0°. *e*) NaCN, AcOH, MnO_2, MeOH, r.t. *f*) SeO_2, *t*-BuOOH, CH_2Cl_2, 5–8°. *g*) $NaBH_4$, EtOH, r.t. *h*) 1) SeO_2, *t*-BuOOH, CH_2Cl_2, 0°; 2) $NaBH_4$, EtOH, 0°. *i*) $(t\text{-Bu})_2Me_2SiCl$, imidazole, DMF. *k*) K_2CO_3, MeOH. *l*) Me_2S, NBS, CH_2Cl_2, –20°. *m*) NaH, BuLi, THF, 0°. *n*) $NaBH_4$, MeOH, 0°. *o*) TsCl, $Me_2NC_5H_4N$, pyridine, 115°. *p*) DBU, 120°. *q*) Bu_4NF, THF.

For radical cyclisation by the vitamin-B_{12}(Cbl)-catalysed, light-assisted electrolysis [12], the starting bromo derivatives were dissolved in 0.3M $LiClO_4$/DMF containing 3–12 mol-% of hydroxocobalamin hydrochloride (= vitamin B_{12a}; with respect to substrate, 100 mol-%) and electrolysed at 15–22° in the cathodic compartment of a divided cell at a carbon electrode at a constant potential of –1.2 V (*vs.* SCE) under irradiation with visible light by a halogen lamp. During reaction, the current stayed at a steady-state level and declined at the end to a background value. The products were then isolated by extraction, separated by chromatography, and analysed by spectroscopic methods. As generally observed in radical reactions, the yield of products strongly depends on the reaction conditions, especially on the relative as well as the absolute concentrations of reagents and intermediates during the whole process.

Cyclisations in the Deca-5,9-dien-1-yl Radical Series. Radical Reactions of Bromo Acetals **12** *and* **13** (see *Scheme 4*). The Cbl-catalysed electrolysis of racemic α-bromo acetal **12** afforded, in 58% yield, a colourless oil consisting mainly (93%, GC) of three racemic compounds: 78% of oxolane **17a** as a 15:1 mixture of *cis/trans*-diastereoisomers and 15% (*E*)-configurated oxolane **17b**. There is no indication for the formation of bicyclic products. The major diastereoisomer of **17a** as well as **17b** are fully characterised by their ^{1}H-NMR, ^{13}C-NMR, and mass spectra and the minor diastereoisomer of **17a** by a MS which is coincident with that of the major isomer. The assignment of the *cis*-configuration to the major (thermodynamically more stable) acetal **17a** is based on NOE experiments: irradiation of one of the two diastereoisotopic H–C(3) causes a NOE on H–C(2) and none on CH_2(1′), whereas irradiation of the other H–C(3) causes a NOE on CH_2(1′) and none on H–C(2).

Scheme 4. *Radical Cyclisation of Bromo Acetals*. Only one enantiomer of the racemic compounds is shown.



a) Electrolysis at −1.2 V (*vs.* SCE) in 0.3M $LiClO_4$/DMF in presence of cat. amounts (3–5 mol-%) of vitamin B_{12a}, VIS light, 15°.

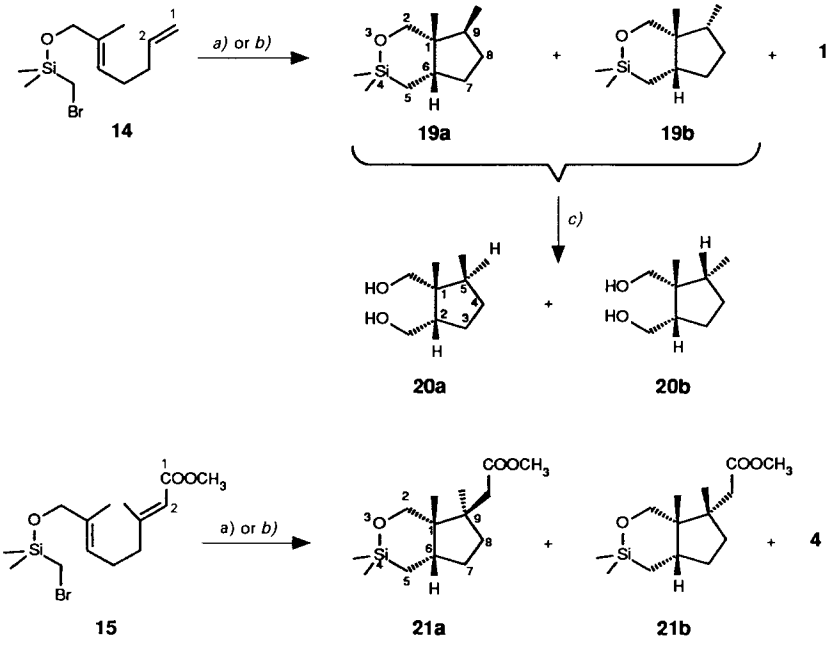
The bromo acetal **13** possesses an α,β-unsaturated ester moiety and is thus a more reactive substrate towards intramolecular attack by a transient nucleophilic radical than **12** with its unactivated terminal C=C bond. Nevertheless, the Cbl-catalysed electrolysis of racemic **13** gave, in 87% yield, only monocyclic oxolanes as a mixture of five racemic compounds: 52% of monoene **18a** (*cis/trans* = 11:1), 4% of diene **18b**, and 34% of β,γ-unsaturated ester **18c** (*cis/trans* = 9:1). All compounds were fully characterised by their ^{1}H-NMR, ^{13}C-NMR and mass spectra. The assignment of the configuration of the predominating *cis*-diastereoisomers of **18a** and **18c** is based on NOE experiments in the same manner as discussed above for **17a**.

The formation of racemic oxolanes in the Cbl-catalysed reaction of the bromo acetals **12** and **13** is explained by kinetically controlled cyclisation of transient 'free' 3-oxadeca-5,9-dien-1-yl radicals. As earlier reported for 3-oxahexen-1-yl-radicals [9], the 5-'*exo-trig*' cyclisation predominates totally over the 6-'*endo*' mode despite of the fact that the initial radical has to attack at the higher alkyl-substituted C-atom of the olefinic bond and although a transient radical, resulting from a potential 6-'*endo*' cyclisation, could have been trapped by intramolecular addition to an (activated) olefinic bond. Conversion of

the monocyclic secondary radicals to products take place formally by uptake of a H-atom to give **17a** and **18a**, by release of a H-atom to give **17b** and **18b**, or by a [1,5]-H shift of an allylic H-atom followed by release of a H-atom to give **18c** (uptake or release of H occur very likely *via* reductive protonation and reductive elimination of intermediate organocobalamins [20]).

Radical Reactions of (Bromomethyl)silyl Ethers **14** *and* **15** (see *Scheme 5*). In sharp contrast to the 5-'*exo*' radical cyclisation of α-bromo acetals **12** and **13**, the corresponding (bromomethyl)silyl ethers **14** and **15** afforded, under radical forming conditions, only bicyclic products **19** and **21** together with variable, but large amounts of the starting

Scheme 5. *Radical Cyclisation of (Bromomethyl)silyl Ethers*. Only one enantiomer of the racemic compounds is shown.



a) Bu_3SnH/AIBN (cat.), benzene, 80°; then evaporation of solvent and chromatography on silica gel. *b*) Electrolysis at −1.2 V (*vs.* SCE) in 0.2M $LiClO_4$/DMF in presence of cat. amounts (12 mol-%) of vitamin B_{12a}, VIS light, 15°; then extraction with Et_2O and chromatography. *c*) KF, H_2O_2 in DMF, 60°.

Table. *Radical Cyclisations of (Bromomethyl)silyl Ethers* **14** *and* **15**

Starting material	Method	Products (% yield with respect to starting material)		
14	Bu_3SnH[a])	**19a** (13)	**19b** (25)	**1** (60)
14	Cbl[b])	**19a** (2)	**19b** (4)	**1** (90)
15	Bu_3SnH[a])	**21a** (15)	**21b** (15)	**4** (64)
15	Cbl[b])	**21a** (7)	**21b** (0)	**4** (91)

[a]) Bu_3SnH, AIBN (cat.), benzene, 80°, then chromatography on silica gel.

[b]) Electrolysis: −1.2 V (*vs.* SCE) in 0.2M $LiClO_4$/DMF, vitamin B_{12a} (cat. 12 mol-%), VIS light, then extraction with Et_2O and chromatography on silica gel.

alcohols **1** and **4**, respectively. Surprisingly, monocyclic compounds resulting from an initial 5-'*exo*' cyclisation could not be detected. Thus, the Bu_3SnH-promoted radical reaction of **14** gave, after chromatography on silica gel, in 60% yield **1** and in *ca.* 40% yield a colourless oil consisting of the two isomeric bicyclic silyl ethers **19a** and **19b** (anal. GC: ratio 1:2; GC/MS: 198 (M^+, $C_{11}H_{22}OSi$) for both compounds). The Cbl-catalysed electrolysis of **14** afforded **19a** and **19b** (ratio 1:2) in much smaller yield (see *Table*). Since **19a** and **19b** could not be isolated separately, their mixture was transformed to the corresponding diols **20a**/**20b** (ratio 1:2) by oxidative silyl-ether cleavage employing H_2O_2/KF as reported by *Tamao* and *Kumada* [21]. The diols were separated by prep. GC and fully characterised by their ^{1}H-NMR, ^{13}C-NMR, and mass spectra. The relative configuration of **20a** and **20b** is based on NOE measurements. The configuration at the cyclopentane ring remains unchanged in the conversion **19** → **20**. Thus, **19** is a *cis*-fused 3-oxa-4-silabicyclo[4.3.0]nonane, the isomers **19a** and **19b** differing only in the configuration at C(9).

For the minor isomer **20a** (originating from **19a**) NOE's were measured between Me–C(1) and H–C(2) as well as between Me–C(1) and 1 H of $HOCH_2$–C(1), no NOE was observed, however, between Me–C(5) and $HOCH_2$–C(1). The major isomer **20b** (originating from **19b**) shows NOE's as **20a**, but additionally also between Me–C(1) and H–C(5) as well as between Me–C(5) and 1 H of at $HOCH_2C(1)$.

The radical reactions of (bromomethyl)silyl ether **15** were carried out under the same conditions as for **14**. The Bu_3SnH-promoted reaction of **15** gave 64% of alcohol **4** and 30% of a mixture of the two bicyclic silyl ethers **21a** and **21b** in a ratio of *ca.* 1:1 (*Scheme 5*, *Table*). The ethers were separated by prep. GC and characterised by ^{1}H-NMR, ^{13}C-NMR, and mass spectroscopy. The Cbl-catalysed reaction of **15** afforded **4** in 91% yield and only one bicyclic compound, **21a**, in 7% yield. The relative configurations of **21a** and **21b** were determined by NOE experiments (see *Exper. Part*). Thus, both isomers are *cis*-fused 3-oxa-4-silabicyclo[4.3.0]nonanes and differ only in the configuration at C(9).

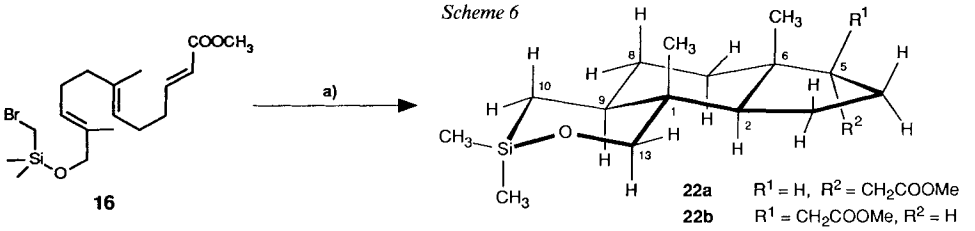
It is well known that the substitution of a methylene group by a dimethylsilyl group adjacent to a radical center causes several effects: *i*) the formation of silyl-substituted C-radicals ($Me_2Si–\dot{C}H_2$) by homolytic cleavage of C–H or C–X bonds is facilitated [22] [23], *ii*) the radical center is 'flattened' (dπ–pπ conjugation) [24], *iii*) the rate of H-abstraction by $Me_2Si–\dot{C}H_2$ from H-donors (like *e.g.* tin hydrides) is an order of magnitude faster than in the case of an unsubstituted C-radical [10b], *iv*) $Me_2Si–\dot{C}H_2$ radicals exhibit a remarkable propensity to undergo kinetically controlled 6-'*endo-trig*' cyclisation (by lowering the rate of the alternative 5-'*exo-trig*' cyclisation) ascribed to the long (1.91 Å) Si–C bond and non-bonded interactions of axial Me groups [10b]. However, it is further known that (bromomethyl)dimethylsilyl ethers of a series of allylic alcohols undergo tin hydride promoted cyclisation preferentially by the 5-'*exo*' mode [10a]. The silyl ether of 2-methylprop-2-en-1-ol (closely related to the substrates of this work) is reported to give, in more than 52% yield, the cyclic 5- and 6-ring silyl ethers in a ratio close to 1:1.8 [10a].

Our observation of the exclusive formation of bicyclic compounds **19** and **21** among the non-polar products of the radical reaction of **14** and **15** (*i.e.* no products resulting from an initial 5-'*exo*' cyclisation) is, therefore, meaningful. If thermodynamic control in the first 6-'*endo*' cyclisation step is excluded [10b], then a concerted 6-'*endo*' → 5-'*exo*' 'tandem' cyclisation, driven by the favourable *cis*-5-'*exo*' closure, has to be taken into account to explain the experimental results. The formation of the alcohols **1** and **4** is very likely the result of a fast radical-type hydrogenolysis of the starting bromides **14** and **15**,

respectively, followed by trimethylsilyl-ether hydrolysis during chromatography on active silica gel.

Cyclisation in the Tetradeca-5,9,13-trien-1-yl Radical Series. Radical Reaction of (Bromomethyl)silyl Ether **16** (see *Scheme 6*). In order to get a first insight into sequential radical reactions of more extended linear polyenes, the (bromomethyl)silyl ether **16** was chosen as starting material. Preliminary experiments using Bu_3SnH/AIBN in benzene gave, along with some unreacted **16** (10%) and alcohol **7** (51%), a mixture of many non-polar products (39%) containing *ca.* 70% (28% with respect to **16**) of the isomers **22a**/**22b** (anal. GC: ratio 2:1; GC/MS: 324 (M^+, $C_{18}H_{32}O_3Si$) for both compounds). Small amounts of **22a** and **22b**, each *ca.* 80% pure, could be obtained by repeated prep. HPLC. Their structures were determined by means of extensive ^1H- and ^{13}C-NMR experiments.

Scheme 6



a) Bu_3SnH/AIBN (cat.), benzene, 80°; then evaporation of solvent and chromatography on silica gel.

The assignment of a few H-resonances was straightforward due to their characteristic chemical shifts and multiplicities. The well separated signals of H_{ax}–C(10) and H_{eq}–C(10) revealed coupling constants with H–C(9) of *ca.* 13 and 3 Hz, respectively, for both **22a** and **22b**, establishing axial orientation of H_{ax}–C(10) and H–C(9). The assignment of H_{ax}–C(13) and H_{eq}–C(13) was based on chemical-shift arguments and the partially resolved long-range coupling of H_{ax}–C(13) with Me–C(1). The assignment of most of the remaining H-resonances, however, was hampered by extensive signal overlap and higher-order effects. To disentangle these resonances and to identify CH and CH_2 signals, a $^{13}C,^1H$ shift correlation experiment with reverse mode of detection and without ^{13}C broad-band decoupling in the detection period was applied [25]. The high sensitivity of this experiment allowed all the expected resonances to be located as cross peaks in the 2D spectrum within reasonable measuring times, despite the low sample amounts available. The unambiguous assignment of the ^1H-signals and the configurational analysis, however, was established by the interpretation of the results of a set of 1D NOE experiments. The axial orientation of Me–C(1) and hence the *trans*-connectivity of the two six-membered rings was proved for **22a** and **22b** by mutual NOE's measured for Me–C(1)/H_{ax}–C(10) and Me–C(1)/H_{eq}–C(13); no mutual NOE's could be detected for Me–C(1)/H_{ax}–C(13). Mutual NOE's measured for H_{ax}–C(13)/H–C(2) and Me–C(1)/Me–C(6) in both compounds, on the other hand, proved the chair conformation of the middle six-membered ring, the axial position of H–C(2) and Me–C(6), and hence the *trans*-connectivity of the six- and five-membered rings. The *trans-transoid-trans*-configuration of the tricyclic system in both compounds was further corroborated by mutual NOE's (see *Exper. Part*). The two compounds, therefore, differ only in the configuration at C(5). Mutual NOE's measured for H–C(2) and MeOOCCH_2–C(5) of **22a** and for H–C(2)/H–C(5) of **22b** allowed the configuration of the side chain at C(5) to be assigned as α and β, respectively.

The reaction **16** → **22** is explained as a 6-'*endo*' → 6-*endo* → 5-'*exo*' sequential radical cyclisation initiated by the generation of the Me_2Si–$\dot{C}H_2$ radical and terminated by a H-transfer to the electrophilic radical in α position to the ester group. The *trans-transoid-trans* ring connection in **22** is that of the thermodynamically most stable tricyclic system. The question remains, therefore, open whether cyclisation occurs under kinetic or thermodynamic control. Sequential cyclisation *via* tertiary-radical intermediates is one possibility; however, a (entropically disfavoured) concerted process, at least guiding the initial 6-'*endo*' addition, is not excluded.

Apart from mechanistic considerations, the radical cyclisation **16** → **22** is nevertheless a fact that may stimulate further research on cyclisation of extended linear polyenes.

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Experimental Part

1. *General.* Chemicals and solvents: Vitamin B_{12a} (= hydroxocobalamine hydrochloride; pyrogen-free *Fr. Ph.BP*, 10.7% loss on drying, < 2% cyanocobalamine) from *Roussel Uclaf;* MnO_2 (precipitated, active, for synthesis) from *Merck;* BuLi (2.4M) and Bu_4NF (1M in THF) from *Aldrich;* all other reagents and solvents from *Fluka: t*-BuOOH 70% in H_2O; SeO_2, DMF, AcOH, CH_2Cl, MeOH, and benzene *puriss p.a.*; other reagents, *purum* grade. The electrochemical experiments were carried out in two different electrochemical cells under otherwise the same potentiostatic conditions: bromo acetals in cell depicted in the *Figure*, (bromomethyl)silyl ethers

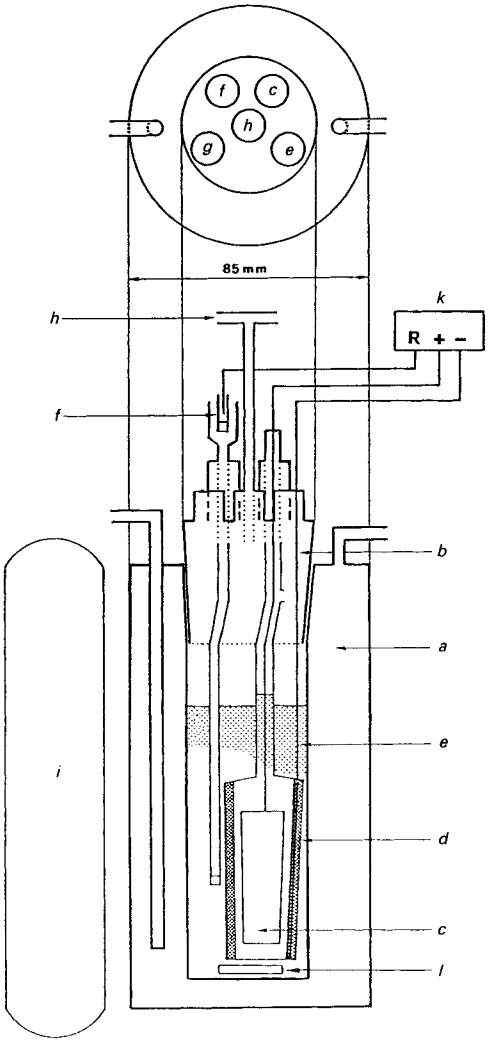

Figure. *Equipment for Electrolysis.*
a) Cylindrical double-wall cell (*Pyrex* glass) with central ground-glass joint (diam. 43 mm) and cooling water in- and outlet.
b) Head with ground-glass joint and five ground-glass necks.
c) Anode compartment: conical *G4* glass frit, medium diam. 20 mm, height 60 mm, content *ca.* 10 ml (sintered to a permeability of 1–2 drops of acetone/min of the filled anode compartment in an acetone-saturated atmosphere) attached to a glass tube (with a hole for pressure equilibration). Anode: cylindrical Pt-sheet (50 × 20 mm) connected by a Pt-wire to the (+)-pole of *k*).
d) Cathode: 1.5 g carbon felt (*Sigratherm felt GFA 5, Sigri Elektrodengraphit GmbH*, D-8901 Meitingen) cut to a trapezium-shaped piece (62 × 55 × 2 mm), wrapped round the conical glass frit and fixed by a *Teflon* thread.
e) Pt-wire (pulled through the carbon felt) and connected to the (−)-pole of *k*).
f) Saturated calomel reference electrode (SCE).
g) Inlet for reagents.
h) Ar bubbler.
i) 250 W halogen lamp cooled by fan.
k) Potentiostat *Amel 550/30 V* with analog integrator *Amel 721* and plotter *Linseis*. All potentials are given with respect to SCE.
l) Magnetic stirring bar.

in cell described in [12c] of *ca.* 60 ml volume and equipped with a *G4* glass frit diaphragm. ^{1}H-NMR: *Varian EM 360L* (60 MHz), *Bruker AC-300* (300 MHz), and *Bruker AM-400WB* (400 MHz), TMS (= 0 ppm) as internal standard. NOE: irradiated H/affected H's. IR: *Perkin-Elmer-782* spectrometer. MS: *Varian-MAT-CH-7A* spectrometer, ionization energy 70 eV. $[\alpha]_D$: *Perkin-Elmer-241* polarimeter. Anal. GC: *Hewlett-Packard-5790* gas chromatograph; 20-m *Duran* glass cap. column coated with *SE-54* (*df* = 0.15 μm), temp. program either from 40–250° or 100–250° at a rate of 3°/min and 5°/min, resp.; flame-ionization detector (FID); purity in % of relative peak intensities; enantioselective GC on 10% heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrine in *OV 1701* (= chiral phase), FID. Prep. GC: *Perkin-Elmer-F21* gas chromatograph; 5% *Carbowax 20 M* on *Chromosorb G-AW-DMCS*, 60–80 mesh, 1 × 43 cm. HPLC: *Altex-100* solvent-metering pump with preparative head, flow rate 0–28 ml/min; *RefractorMonitor LDC 1107* refractive index detector and *Uvikon 720 LC* UV/VIS detector; silical gel *DuPont*, 7 μm, 23 mm × 250 mm; silica gel *LiChrosorb Si 60* from *Merck*, 5 μm, 10 mm × 250 mm. TLC: precoated plates, silica gel *60* F_{254} from *Merck*, detection with H_2SO_4/vanilline. Flash chromatograph (FC): silica gel for FC from *Baker*.

2. *Allylic Alcohols. (2E)-2-Methylhepta-2,6-dien-1-ol* (**1**) [14]. To a mixture of Mg (3.47 g, 142.8 mmol) and dry THF (6 ml), treated with a small amount of I_2, was added under N_2 at 0° allyl chloride (5.46 g, 71.4 mmol) in dry THF (10 ml) within 1 h 50 min. Then the mixture was refluxed for 45 min. The black soln., filtered through a *G2* frit in a dropping funnel, was added to a suspension of epoxide **3** [13] (4.46 g, 47.6 mmol) and CuI (0.45 g, 2.4 mmol) in dry THF (150 ml) at −35° to −25° within 2 h. The mixture was stirred at −25° for 1 h. After hydrolysis with sat. NH_4Cl/H_2O (80 ml) at −25°, the aq. layer was extracted with Et_2O (3 × 50 ml). The org. extracts were washed with sat. $NaHCO_3$, soln. brine, and H_2O (2 ×), dried (Na_2SO_4), and evaporated. The remaining yellow oil was distilled over a micro split-tube column (*Fisher MMS 202*, b.p. 63.0–65.7°/7 mbar): 4.90 g (82%) of **1** ((*E*/*Z*) 23:1). Colourless oil. R_f 0.27 (Et_2O/pentane 2:5). GC (*SE-54*, 20 m, 40–250°, 3°/min): R_t 11.1 (4% of (*Z*)-isomer), R_t 11.9 (91% of (*E*)-isomer). IR (film): 3330*s* (br.), 3080*m*, 2980*s*, 2920*s*, 2860*s*, 1830*w*, 1675*w*, 1640*s*, 1440*s*, 1225*w*, 1005*s*, 910*s*, 850*m*, 640*m*. ^{1}H-NMR (300 MHz, $CDCl_3$; signals of the (*E*)-isomer): 5.90–5.74 (*m*, H–C(6)); 5.46–5.38 (*m*, H–C(3)); 5.08–4.99, 4.99–4.94 (2*m*, CH_2(7)); 4.01 (*s*, CH_2(1)); 2.20–2.08 (*m*, CH_2(4), CH_2(5)); 1.67 (br. *s*, Me–C(2)); 1.47–1.35 (br. *s*, OH); selected signals of the (*Z*)-isomer: 4.12 (*s*, CH_2(1)); 1.81 (br. *s*, Me–C(2)). ^{13}C-NMR (75 MHz, $CDCl_3$; signals of the (*E*)-isomer): 138.4 (C(6)); 135.2 (C(2)); 125.5 (C(3)); 114.7 (C(7)); 68.9 (C(1)); 33.6 (C(5)); 27.0 (C(4)); 13.7 (*C*H_3–C(2)). MS: 126 (< 1, M^+), 111 (6), 108 (36), 95 (28), 93 (57), 67 (46), 57 (35), 53 (32), *43* (100), 41 (55), 29 (27), 18 (49).

(2E)-Methyl 3,7-Dimethylocta-2,6-dienoate (**6**) [15]. To a mixture of active MnO_2 (105.80 g, 1.22 mol) in hexane (250 ml) was added geraniol (**5**), (9.20 g, 59.7 mmol) in hexane (50 ml) at 0°. The suspension was stirred at 0° for 45 min. After filtration, the solvent was evaporated. The residue was added to a mixture of NaCN (15.09 g, 0.31 mol), AcOH (5.52 g, 92.0 mmol), and MnO_2 (105.80 g, 1.22 mol) in MeOH (250 ml) and stirred at r.t. for 15 h. The solid was filtered off, the solvent evaporated. The residue diluted with H_2O and extracted with Et_2O (5 × 50 ml), and the extract washed with brine and H_2O (2 ×), dried (Na_2SO_4), and evaporated. FC (Et_2O/pentane 1:40, silica gel) of the crude material yielded 6.54 g (60%) of **6** as colourless oil with R_f 0.35. GC (*SE-54*, 20 m, 40–250°, 3°/min): R_t 25.1 (purity 99%). IR (film): 2960*s*, 2860*m*, 1725*s*, 1650*s*, 1435*s*, 1385*s*, 1360*s*, 1330*m*, 1280*m*, 1225*s*, 1150*s*, 1110*m*, 1060*m*, 1030*w*, 865*m*, 730*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.67 (*m*, H–C(2)); 5.11–5.03 (*m*, H–C(6)); 3.68 (*s*, COOMe); 2.18–2.14 (*m*, CH_2(4), CH_2(5), Me–C(3)); 1.68 (*s*, Me–C(7)); 1.61 (*s*, Me(8)). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.3 (C(1)); 160.1 (C(3)); 132.5 (C(7)); 123.0 (C(6)); 115.2 (C(2)); 50.8 (COO*C*H_3); 41.0 (C(5)); 26.1 (C(4)); 25.7 (C(8)); 18.8 (*C*H_3–C(3)); 17.7 (*C*H_3–C(7)). MS: 182 (1, M^+), 151 (5), 150 (2), 139 (5), 123 (16), 122 (8), 114 (24), 83 (23), 82 (10), *69* (100), 67 (9), 41 (68), 28 (28), 18 (33).

(2E,6E)-Methyl 8-Hydroxy-3,7-dimethylocta-2,6-dienoate (**4**). To a soln. of SeO_2 (1.67 g, 14.8 mmol) in dry CH_2Cl_2 (40 ml) was added 70% *tert*-butyl peroxide in H_2O (16.2 ml, 116.6 mmol) at 0° in the dark. After stirring at 0° for 30 min, **6** (5.40 g, 29,7 mmol) in CH_2Cl_2 (10 ml) was added at 0–5° within 15 min, and the mixture was stirred at 5–8° for 18 h. CH_2Cl_2 (50 ml) was added, the soln. washed with sat. $NaHCO_3$ soln. (2 ×) and brine (2 ×), dried (Na_2SO_4), and evaporated. For reduction of some aldehyde, a soln. of $NaBH_4$ (0.11 g) in dry EtOH (20 ml) was added and the mixture kept at 0° for 45 min (TLC control). EtOH was removed *i.v.* and the residue diluted with H_2O (50 ml) and extracted with Et_2O (4 × 40 ml). The combined org. phases were washed with brine, dried (Na_2SO_4), and evaporated FC of the oil (Et_2O/pentane 1:1, silica gel) yielded 3.59 g (61%) of **4**. R_f 0.31. GC (*SE-54*, 20 m, 40–250°, 3°/min): R_t 36.6 (purity 96%). IR (film): 3410*s* (br.), 2950*s*, 2860*m*, 1720*s*, 1650*s*, 1435*s*, 1385*m*, 1360*m*, 1230*s*, 1150*s*, 1060*m*, 1020*m*, 865*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.69–5.66 (*m*, H–C(2)); 5.41–5.33 (*m*, H–C(6)); 4.00 (br. *d*, *J* = 5.8, CH_2(8)); 3.69 (*s*, COOMe); 2.30–2.19 (*m*, CH_2(4), CH_2(5)); 2.17 (*d*, *J* = 1.3, Me–C(3)); 1.67 (br. *s*, Me–C(7)); 1.48 (*t*, *J* = 5.8, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.2 (C(1)); 159.6 (C(3)); 135.9 (C(7)); 124.3 (C(6)); 115.5 (C(2)); 68.7 (C(8)); 50.8 (COO*C*H_3); 40.5 (C(5)); 25.5(C4)); 18.8 (*C*H_3–C(3)); 13.7 (*C*H_3–C(7)). MS: 198 (1, M^+), 180 (10), 166 (9), 148 (9), 138 (8), 121 (41), *114* (100), 83 (98), 82 (48), 43 (77), 41 (20).

(2E,6E)-8-Hydroxy-3,7-dimethylocta-2,6-dien-1-yl Acetate (**9a**). SeO_2 (3.84 g, 34.6 mmol) was suspended in CH_2Cl_2 (60 ml). The suspension was cooled to 0° and light excluded. Then, 70% *tert*-butyl peroxide in H_2O (30.6 ml, 220.2 mmol) was added gradually to the cooled suspension at 0 to 2°. The mixture was stirred at 0° for 30 min, and then geranyl acetate (**8**; 11.2 g, 57 mmol) in CH_2Cl_2 (15 ml) was added portionwise. After stirring at 4° for 20 h, benzene (60 ml) was added and the solvent removed *i.v.* The residue was dissolved in AcOEt (70 ml), washed successively with 1M NaOH (3 × 50 ml) and brine, and dried ($MgSO_4$). The solvent was evaporated and the resulting oil purified by FC (AcOEt/pentane 1:4, 300 g silica gel). Chromatography yielded 5.23 g of **9a** and 3.02 g of the corresponding aldehyde. The aldehyde was dissolved in EtOH (30 ml) and $NaBH_4$ (180 mg) added portionwise at 0°. H_2O (3 ml) was then added to the mixture and the EtOH removed *i.v.* The residue was extracted with AcOEt (50 ml) and the org. phase washed with brine, dried ($MgSO_4$), and evaporated: 2.38 g of **9a**. The combined alcohol fractions were distilled in a 'Kugelrohr' (140°/5·10^{-3} mbar): 7.61 g (63%) of **9a**. Colourless oil. GC (*SE-54*, 20 m, 40–250°, 3°/min): R_t 38.4 (purity 90%). IR (CCl_4): 3620*m*, 3050–2820*m*, 1735*s*, 1450*w*, 1380*m*, 1370*m*, 1020*m*, 950*w*, 910*w*. ^{1}H-NMR (60 MHz, $CDCl_3$): 5.60–5.20 (*m*, H–C(6), H–C(2)); 4.63 (*d*, *J* = 7.5, CH_2(1)); 4.05 (*s*, CH_2(8)); 2.30–2.00 (*m*, CH_2(4), CH_2(5)); 2.05 (*s*, COOMe); 1.78–1.55 (*m*, Me–C(7), Me–C(3), OH). MS: 152 (3), 137 (3), 134 (15), 121 (6), 119 (7), 95 (6), 94 (11), 93 (9), 85 (11), 84 (51), 69 (9), 68 (59), 67 (22), 55 (9), *43* (100), 41 (13).

*(2E,6E)-8-[(*tert*-Butyl)dimethylsilyloxy]-3,7-dimethylocta-2,6-dien-1-yl Acetate* (**9b**). A soln. of **9a** (7.41 g, 35 mmol), (*t*-Bu)Me_2SiCl (8.97 g, 59 mmol), and imidazole (7.15 g, 105 mmol) in DMF (25 ml) was stirred at r.t. for 24 h. The mixture was dissolved in pentane (200 ml) and washed with H_2O (3 × 100 ml), dried ($MgSO_4$), and evaporated. The resulting oil was purified by FC (AcOEt/pentane 1:9, 200 g, silica gel): 10.31 g (90%) of **9b**. Colourless oil. GC: (*SE-54*, 20 m, 40–250°, 3°/min): R_t 50.1 (purity 90%). IR (CCl_4): 3050*m*, 2985*m*, 2960*m*, 2930*m*, 2860*m*, 1735*s*, 1420*m*, 1370*w*, 1270*s*, 1110*w*, 1060*m*, 910*w*, 895*m*, 835*s*. ^{1}H-NMR (60 MHz, $CDCl_3$): 5.60–5.20 (*m*, H–C(6), H–C(2)); 4.63 (*d*, *J* = 7.5, CH_2(1)); 4.05 (*s*, CH_2(8)); 2.30–2.00 (*m*, CH_2(4), CH_2(5)); 2.05 (*s*, COOMe); 1.75, 1.65 (2*s*, Me–C(7), Me–C(3)); 0.90 (*s*, (*t*-Bu)Si); 0.05 (2*s*, Me_2Si). MS: 209 (1), 201 (1), 199 (3), 198 (3), 159 (2), 141 (3), 135 (17), *117* (100), 107 (13), 93 (23), 75 (27), 73 (19), 43 (6).

*(2E,6E)-8-[(*tert*-Butyl)dimethylsilyloxy]-3,7-dimethylocta-2,6-dien-1-ol* (**9c**). To a soln. of **9b** (10.31 g, 31.6 mmol) in MeOH (20 ml), K_2CO_3 (10.8 g) was added and stirred at r.t. for 1 h. After dilution with H_2O (20 ml), the MeOH was removed *i.v.* and the aq. residue extracted with AcOEt. The extract was washed with brine and H_2O, dried ($MgSO_4$), and evaporated: 7.54 g (84%) of **9c**. Colourless oil. GC (*SE-54* 20 m, 40–250°, 3°/min): R_t 45.7 (purity 95%). IR (CCl_4): 3610*m*, 3050*s*, 2985*s*, 2960*s*, 2935*s*, 2860*s*, 1670*w*, 1420*s*, 1105*m*, 1060*m*, 895*s*, 835*s*. ^{1}H-NMR (60 MHz, $CDCl_3$): 5.70–5.30 (*m*, H–C(2), H–C(6)); 4.20 (*d*, *J* = 7.5, CH_2(1)); 4.05 (*s*, CH_2(8)); 2.35–2.05 (*m*, CH_2(4), CH_2(5)); 1.75, 1.65 (2*s*, Me–C(7), Me–C(3)); 1.50 (br. *s*, OH); 0.95 (*s*, (*t*-Bu)Si); 0.05 (*s*, Me_2Si). MS: 227 (2), 199 (1), 189 (2), 160 (5), 159 (43), 142 (21), 135 (17), 117 (5), 107 (14), 95 (12), 93 (22), *75* (100), 73 (30).

*(2E,6E)-1-Bromo-8-[(*tert*-butyl)dimethylsilyloxy]-3,7-dimethylocta-2,6-diene* (**10**). *n*-Bromosuccinimide (7.10 g, 40 mmol) in CH_2Cl_2 (120 ml) was cooled to 0°. Me_2S (4.5 ml) was then added dropwise (→yellow soln.), the soln. cooled to −25°, and **9c** (11.34 g, 40 mmol) in CH_2Cl_2 (10 ml) added gradually within 30 min. The soln. was warmed to 0° and stirred for 3 h. H_2O/ice (100 ml) was added and the org. phase separated, filtered through neutral Alox (5 g, deactivated with 1 ml H_2O/5 g Alox), and evaporated. The resulting oily **10** was immediately used in the next reaction (due to instability). ^{1}H-NMR (400 MHz, $CDCl_3$): 5.55–5.48, 5.35–5.30 (2*m*, H–C(2), H–C(6)); 4.00 (*d*, *J* = 8.7, CH_2(1)); 3.98 (*s*, CH_2(8)); 2.18–2.04 (*m*, CH_2(4), CH_2(5)); 1.71 (*d*, *J* = 1.4, Me–C(7)); 1.57 (*d*, *J* = 1.2, Me–C(3)); 0.88 (*s*, (*t*-Bu)Si); 0.04 (*s*, Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 143.2 (C(3)); 134.9 (C(7)); 123.3, 120.7 (C(2), C(6)); 68.5 (C(8)); 39.3 (C(1)); 29.5, 25.7 (C(4), C(5)); 26.0 ([(CH_3)$_3$C]Si); 18.5 ([(CH_3)$_3$*C*]Si); 16.0, 13.5 (CH_3–C(3), CH_3–C(7)); −5.1 ((CH_3)$_2$Si).

*(6E,10E)-Methyl 12-[(*tert*-Butyl)dimethylsilyloxy]-7,11-dimethyl-3-oxododeca-6,10-dienoate* (**11a**). To a suspension of NaH (2 g, 55% suspension in oil, 40 mmol) in dry THF (50 ml) at 0°, methyl acetoacetate (4.3 ml, 39 mmol) was added dropwise and stirred for 30 min. Then, 2.4M BuLi in hexane (16.3 ml, 39 mmol) was added gradually at 0 to 2°. All crude **10** (*ca.* 40 mmol; from the preceding reaction) was dissolved in THF/pentane (2:1, 15 ml) and added slowly to the yellow soln. at 0–2°. After stirring at 0° for 1 h, 1M HCl (10 ml) was carefully added, maintaining the temp. at 0°. The soln. was diluted with Et_2O (100 ml), the org. phase washed with H_2O (3 × 50 ml), dried ($MgSO_4$), and evaporated, and the resulting oil submitted to FC (AcOEt/pentane 1:9, 300 g silica gel): 6.44 g (44% with respect to **9c**) of **11a**. Colourless oil. GC (*SE-54*, 20 m, 100–250°, 3°/min): R_t 32.6 (purity 96%). IR (CCl_4): 2960*s*, 2930*s*, 2860*s*, 1748*s*, 1715*s*, 1440*m*, 1260*m*, 835*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.36–5.28 (*m* (*t*-like), H–C(10)); 5.09–5.02 (*m* (*t*-like), H–C(6)); 3.96 (*s*, CH_2(12)); 3.71 (*s*, COOMe); 3.42 (*s*, CH_2(2)); 2.54 (*t*, *J* = 7.3, CH_2(4)); 2.30–2.21 (*m* (*q*-like), CH_2(5)); 2.12–2.03, 2.01–1.93 (2*m*, CH_2(8), CH_2(9)); 1.58, 1.55 (2*s*, Me–C(7), Me–C(11)); 0.88 (*s*, (*t*-Bu)Si); 0.03 (*s*, Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 202.5 (C(3)); 167.6 (C(1)); 136.6,

134.4 (C(7), C(11)); 124.1, 122.1 (C(6), C(10)); 68.6 (C(12)); 52.3 ($COOCH_3$); 49.1 (C(2)); 43.0 (C(4)); 39.3 (C(8)); 26.0 (C(9)); 25.9 ([$(CH_3)_3C$]Si); 22.1 (C(5)); 18.4 ([$(CH_3)_3C$]Si); 15.9, 13.4 (CH_3–C(7), CH_3–C(11)); −5,3 ($(CH_3)_2$Si). MS: 326 (2), 325 (10), 308 (3), 307 (12), 233 (9), 203 (32), 199 (6), 198 (6), 174 (14), *173* (100), 171 (8), 159 (23), 141 (12), 135 (24), 107 (22), 105 (19), 93 (28), 89 (30), 81 (20), 75 (61), 73 (73).

*(6*E*,10*E*)-Methyl 12-[(*tert*-Butyl)dimethylsilyloxy]-3-hydroxy-7,11-dimethyldodeca-6,10-dienoate* (**11b**). To a soln. of **11a** (3.00 g, 7.8 mmol) in MeOH (25 ml) at 0°, $NaBH_4$ (250 mg, 6.6 mmol) was added portionwise and stirred at 0° for 30 min. H_2O (8 ml) was added and MeOH removed *i.v.* The aq. soln. was extracted with AcOEt (100 ml) and the org. phase washed with brine, dried ($MgSO_4$), and evaporated: 2.77 g (92%) of **11b**. Colourless oil. GC: dec. on heating block. IR (CCl_4): 3550*w* (br.), 2960*s*, 2930*s*, 2860*s*, 1725*s*, 1255*m*, 1060*m*, 835*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.35–5.28 (*m* (*t*-like), H–C(19)); 5.16–5.09 (*m* (*t*-like), H–C(6)); 4.00–3.94 (*m*, H–C(3)); 3.96 (*s*, CH_2(12)); 3.67 (*s*, COOMe); 2.88 (*d*, J = 3.7, OH); 2.47, 2.39 (*AB* of *ABX*, J_{AB} = 16.2, J_{AX} = 8.7, J_{BX} = 3.7, CH_2(2)); 2.10–1.95 (*m*, CH_2(5), CH_2(8), CH_2(9)); 1.57, 1.54 (2*s*, Me–C(7), Me–C(11)); 1.55–1.39 (*m*, CH_2(4)); 0.88 (*s*, (*t*-Bu)Si); 0.03 (*s*, Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 173.3 (C(1)); 135.8, 134.4 (C(7), C(11)); 124.2, 123.6 (C(6), C(10)); 68.6 (C(12)); 67.6 (C(3)); 51.7 ($COOCH_3$); 41.1, 36.5 (C(2), C(4)); 39.3 (C(8)); 26.1 (C(9)); 25.9 ([$(CH_3)_3$C]Si); 23.9 (C(5)); 18.4 ([$(CH_3)_3C$]Si); 15.9, 13.4 (CH_3–C(7), CH_3–C(11)); −5.3 ($(CH_3)_2$Si). MS: 309 (3), 277 (1), 253 (1), 241 (2), 198 (3), 161 (13), 141 (13), 119 (14), 107 (29), 93 (44), *75* (100), 73 (69), 55 (28), 43 (42).

*(2*E*,6*E*,10*E*)-Methyl 12-[(*tert*-Butyl)dimethylsilyloxy]-7,11-dimethyldodeca-2,6,10-trienoate* (**7a**). To a soln. of **11b** (2.43 g, 6.3 mmol) in pyridine (25 ml), 4-(dimethylamino)pyridine (0.5 g, 4 mmol) and TsCl (1.73 g, 9 mmol) were added and the mixture heated at reflux for 7 h. The cooled mixture was dissolved in AcOEt (150 ml), washed successively with 1M HCl, sat. $NaHCO_3$ soln., and brine (each *ca.* 50 ml), and dried ($MgSO_4$) and the solvent removed *i.v.* The oil obtained (TLC and ^{1}H-NMR: mixture of **7a** and the corresponding β-chloro ester) was dissolved in 1,5-diazabicyclo[5.4.0]undec-5-ene (10 ml) and heated at 120° for 24 h. The cooled mixture was dissolved in AcOEt (100 ml), washed with 1M HCl, sat. $NaHCO_3$ soln. and brine (each *ca.* 50 ml), and dried ($MgSO_4$) and the solvent removed *i.v.* The oil obtained was purified by FC (toluene, 300 g silica gel; then AcOEt/pentane 1:30, 100 g silica gel): 1.03 g (44%) of **7a**. Colourless oil. GC (*SE-54*, 20 m, 100–250°, 3°/min): R_t (41.0 (90% purity). IR ($CHCl_3$): 2960*s*, 2930*s*, 2860*s*, 1725*s*, 1660*w*, 1475*m*, 1440*m*, 1255*m*, 835*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.96 (*td*, J = 15.7, 6.7, H–C(3)); 5.81 (*td*, J = 15.7, 1.5, H–C(2)); 5.37–5.33 (*m* (*t*-like), H–C(10)); 5.12–5.09 (*m* (*t*-like), H–C(6)); 4.00 (*s*, CH_2(12)); 3.71 (*s*, COOMe); 2.25–1.98 (*m*, CH_2(4), CH_2(5), CH_2(8), CH_2(9)); 1.59, 1.58, (2*s*, Me–C(7), Me–C(11)); 0.89 (*s*, (*t*-Bu)Si); 0.04 (*s*, Me_2Si). MS: 310 (2), 309 (7, [M − (*t*-Bu)]$^+$), 278 (0.5), 277 (2), 209 (1.6), 199 (2), 198 (2.5), 185 (4.6), 135 (15), 107 (18), 93 (25), 89 (41), *75* (100), 73 (63), 67 (12), 55 (25), 43 (22), 41 (30).

*(2*E*,6*E*,10*E*)-Methyl 12-Hydroxy-7,11-dimethyldodeca-2,6,10-trienoate* (**7b**). To a soln. of **7a** (400 mg, 1 mmol) in THF (5 ml), 1M Bu_4NF in THF (1.2 ml) was added and stirred for 1.5 h. After dilution with Et_2O, the org. phase was washed with 1M HCl and H_2O, dried ($MgSO_4$), and evaporated. The residue was purified by FC (AcOEt/pentane 1:3, 80 g silica gel). Chromatography yielded 230 mg (85%) of **7b** as a colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.97 (*td*, J = 15.7, 6.7, H–C(3)); 5.83 (*td*, J = 15.7, 1.5, H–C(2)); 5.41–5.35 (*m* (*t*-like), H–C(10)); 5.15–5.09 (*m* (*t*-like), H–C(6)); 4.00 (*s*, CH_2(12)); 3.71 (*s*, COOMe); 2.28–2.01 (*m*, CH_2(4), CH_2(5), CH_2(8), CH_2(9)); 1.81 (br. *s*, OH); 1.66, 1.60 (2*s*, Me–C(7), Me–C(11)). ^{13}C-NMR (100 MHz, $CDCl_3$): 167.2 (C(1)); 149.3 (C(3)); 136.0 (C(7)); 134.9 (C(11)); 125.4, 123.0, 121.0 (C(2), C(6), C(10)); 68.7 (C(12)); 51.3 ($COOCH_3$); 39.1 (C(8)); 32.3 (C(4)); 26.4 (C(9)); 25.9 (C(5)); 16.0, 13.6 (CH_3–C(7), CH_3–C(11)). MS: 235 (0.2), 234 (0.4, [M − H_2O]$^+$), 220 (0.3), 219 (0.4), 202 (0.3), 175 (1.5), 167 (0.8), 161 (1.4), 151 (4), 135 (13), 121 (6), 107 (34), 100 (48), 93 (40), 91 (20), 81 (30), 79 (29), 69 (33), 68 (30), 67 (22), 55 (63), 53 (18), *43* (100), 41 (55), 39 (19).

3. *Synthesis and Cyclisation of Bromo Acetales. (*E*)-7-(2'-Bromo-1'-ethoxyethoxy)-6-methylhepta-1,5-diene* (**12**). To a stirred soln. of **1** (1.50 g, 11.9 mmol) and ethyl vinyl ether (2.57 g, 35.7 mmol) in dry CH_2Cl_2 (20 ml) was added within 30 min under N_2 at −20 to −40° *N*-bromosuccinimide (2.12 g, 11.9 mmol) in portions. The mixture was stirred at −35° for 1 h and then at r.t. for additional 40 min. The precipitate was filtered off and washed with CH_2Cl_2. The combined filtrates were evaporated and the remaining oil submitted to FC (Et_2O/pentane 1:20): 2.48 g (75%) of **12**. Colourless oil. R_f 0.42. GC (*SE-54*, 20 m, 100–250°, 3°/min): R_t 15.9 (purity 97%). IR (film): 3080*w*, 2980*s*, 2925*s*, 1640*m*, 1445*m*, 1375*m*, 1345*m*, 1185*w*, 1120*s*, 1060*s*, 1035*s*, 910*m*, 680*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.85–5.74 (*m*, H–C(2)); 5.45–5.40 (*m*, H–C(5)); 5.03–4.97, 4.96–4.93 (2*m*, CH_2(1)); 4.65 (*t*, J = 5.4, H–C(1')); 4.01, 3.92 (*AB*, J_{AB} = 11.3, CH_2–C(7)); 3.66, 3.56 (*AB* of ABX_3, J_{AB} = 9.3, J_{AX} = J_{BX} = 7.1, CH_3CH_2O); 3.36 (*d*, J = 5.4, CH_2(2')); 2.23–2.02 (*m*, CH_2(4), CH_2(3)); 1.66 (*s*, Me–C(6)); 1.22 (*t*, J = 7.1, CH_3CH_2O). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.3 (C(2)); 131.9 (C(6)); 128.5 (C(5)); 114.8 (C(1)); 100.5 (C(1')); 73.0 (C(7)); 62.3 (CH_3CH_2); 33.4 (C(3)); 31.9 (C(2')); 27.1 (C(4)); 15.2 (CH_3CH_2O); 14.1 (CH_3–C(6)). MS: 197 (< 1), 183 (1), *153* (100), *151* (100), 125 (91), 123 (90), 109 (63), 72 (40), 67 (69), 55 (28), 43 (20), 41 (23).

Cbl-Catalysed Electrolysis of **12**: *(±)-(2*RS,*4*RS*)- and (±)-(2*RS,*4*SR*)-2-Ethoxy-4-methyl-4-(pent-4'-en-1'-yl)oxolane* (**17a** and **17a'**, resp.) *and (±)-(2*RS,*4*RS,*1'*E*)-2-Ethoxy-4-methyl-4-(penta-1',4'-dien-1'-yl)oxolane* (**17b**). To the cathode compartment of an electrochemical cell (see *Fig.*), containing C-felt (*ca.* 0.7 g) as cathode material and 0.3M $LiClO_4$/DMF (70 ml) as solvent, was added vitamin B_{12a} (254 mg, 183 μmol, 2.6 mol-% with respect to **12**). The anode compartment was charged with 0.3M $LiClO_4$/DMF (7 ml). Vitamin B_{12} was reduced to Co^I at −1.2 V (*vs.* SCE) until the current had dropped to a constant level of *ca.* 1.7 mA and the colour had changed from red to dark green. Then **12** (1.95 g, 7.04 mmol) was added by syringe, whereby the colour of the catholyte changed to red. Electrolysis was continued at −1.2 V under irradiation with a 500-W halogen lamp and cooling to *ca.* 16–25°. The current of initially *ca.* 34 mA gradually dropped and reached after 16 h a constant level of *ca.* 10 mA. The reaction was followed by GC, and by end of the electrolysis, all **12** was consumed. The soln. was poured into ice/H_2O and extracted with Et_2O (5 × 60 ml). The org. soln. was washed with brine, dried ($NaSO_4$), and evaporated. The crude oil was purified by FC (Et_2O/pentane 1:20, silica gel): 0.81 g (58%; calc. as $C_{12}H_{22}O_2$ with resp. to **12**) with R_f 0.29. GC (*SE-54*, 20 m, 40–250°, 3°/min): 15% of **17b**, R_t 23.0; 73% of **17a**, R_t 23.3; 5% of **17a'**, R_t 23.7; 5% of 2 fractions of unknown compounds at higher R_t. For spectroscopic analysis, the mixture was separated by prep. HPLC (silica gel (*DuPont*), 7 μm, 23 mm × 250 mm; hexane/(*t*-Bu)MeO 98:2, flow rate 14 ml/min; detection by refractometer) to give 2 main fractions, **17a**/**17a'** and **17b**.

17a/**17a'** (*cis*/*trans* 15:1): Anal. GC (chiral phase): 1:1 ratio for the enantiomers of both **17a** and **17a'**. ^{1}H-NMR (400 MHz, $CDCl_3$; data of the prevailing *cis*-epimer): 5.86–5.73 (*m*, H–C(4')); 5.17 (*X* of *ABX*, H–C(2)); 5.03–4.97, 4.96–4.93 (2*m*, CH_2(5')); 3.75, 3.48 (*AM* of *AMX*, J_{AM} = 9.6, $J_{AX} = J_{MX}$ = 7.1, CH_3CH_2O); 3.63, 3.48 (*AB*, J_{AB} = 8.1, CH_2(5)); 2.08–1.99 (*m*, CH_2(3')); 1.89, 1.66 (*AB* of *ABX*, J_{AB} = 13.2, J_{AX} = 5.8, J_{BX} = 3.6, CH_2(3)); 1.51–1.30 (*m*, CH_2(2'), CH_2(1')); 1.20 (*t*, *J* = 7.1, CH_3CH_2O); 1.04 (*s*, Me–C(4)). ^{13}C-NMR (100 MHz, $CDCl_3$; data of the prevailing *cis*-epimer): 138.7 (C(4')); 114.6 (C(5')); 104.7 (C(2)); 77.7 (C(5)); 63.2 (CH_3CH_2O); 46.2 (C(3)); 42.5 (C(4)); 38.8 (C(1')); 34.4 (C(3')); 24.9, 24.9 (C(2'), CH_3–C(4)); 15.3 (CH_3CH_2O). GC/MS (*SE-54*; identical MS for **17a'** and **17a**): 198 (< 1, M^+), 197 (< 1, $[M - H]^+$), 169 (1), 153 (7), 135 (8), 125 (7), 109 (20), 99 (31), *83* (100), 67 (43), 55 (75), 41 (59).

17b: ^{1}H-NMR (400 MHz, $CDCl_3$): 5.86–5.75 (*m*, H–C(4')); 5.59 (*td*, *J* = 15.7, 1.2, H–C(1')); 5.47 (*td*, *J* = 15.7, 6.3, H–C(2')); 5.20 (*X* of *ABX*, H–C(2)); 5.05–4.99, 5.01–4.97 (2*m*, CH_2(5')); 3.76, 3.45 (*AM* of AMX_3, J_{AM} = 9.6, $J_{AX} = J_{MX}$ = 7.1, CH_3CH_2O); 3.72, 3.47 (*AX*, J_{AX} = 8.1, CH_2(5)); 2.79–2.73 (*m*, CH_2(3')); 1.96, 1.83 (*AB* of *ABX*, J_{AB} = 13.4, J_{AX} = 5.6, J_{BX} = 3.7, CH_2(3)); 1.21 (*t*, *J* = 7.1, CH_3CH_2O); 1.16 (*s*, Me–C(4)). ^{13}C-NMR (100 MHz, $CDCl_3$): 137.0, 136.4 (C(4'), C(1')); 126.1 (C(2')); 115.1 (C(5')); 104.7 (C(2)); 77.0 (C(5)); 63.3 (CH_3CH_2O); 46.8 (C(3)); 44.5 (C(4)); 36.7 (C(3')); 24.5 (CH_3–C(4)); 15.3 (CH_3CH_2O). GC/MS (*SE-54*): 166 (3), 151 (4), 135 (7), 125 (60), 120 (14), 105 (11), *97* (100), 91 (30), 79 (56), 67 (39), 55 (45), 41 (59).

*(2*E,*6*E*)-Methyl 8-(2'-Bromo-1'-ethoxyethoxy)-3,7-dimethylocta-2,6-dienoate* (**13**). To a stirred soln. of **4** (1.50 g, 7.6 mmol) and ethyl vinyl ether (1.63 g, 22.6 mmol) in dry CH_2Cl_2 (20 ml) was added within 20 min under N_2 at −20 to −40° *N*-bromosuccinimide (1.35 g, 7.6 mmol) in portions. The mixture was stirred at −30° for 1 h and then at r.t. for additional 3 h. The precipitate was filtered off and washed with CH_2Cl_2. The combined filtrates were evaporated and the remaining oil submitted to FC (Et_2O/pentane 1:6, silica gel): 2.24 g (85%) of **13**. Colourless oil. R_f 0.45. GC (*SE-54*, 20 m, 40–250°, 3°/min): R_t 54.8 (purity 95%). IR (film): 2980*s*, 2950*s*, 2880*s*, 1725*s*, 1650*s*, 1435*s*, 1390*m*, 1360*m*, 1280*w*, 1225*s*, 1190*w*, 1145*s*, 1060*s*, 920*w*, 865*m*, 730*w*, 680*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.69–5.66 (*m*, H–C(2)); 5.44–5.38 (*m*, H–C(6)); 4.67 (*t*, *J* = 5.5, H–C(1')); 4.02, 3.93 (*AB*, J_{AB} = 11.5, CH_2(8)); 3.69 (*s*, COOMe); 3.68, 3.58 (*AB* of ABX_3, J_{AB} = 9.3, $J_{AX} = J_{BX}$ = 7.0, CH_3CH_2O); 3.38 (*d*, *J* = 5.5, CH_2(2')); 2.28–2.18 (*m*, CH_2(4), CH_2(5)); 2.17 (*d*, *J* = 1.3, Me–C(3)); 1.69 (*s*, Me–C(7)); 1.24 (*t*, *J* = 7.0, CH_3CH_2O). ^{13}C-NMR (100 MHz, $CDCl_3$): 167.0 (C(1)); 159.4 (C(3)); 132.6 (C(7)); 127.1 (C(6)); 115.4 (C(2)); 100.6 (C(1')); 72.6 (C(8)); 62.3 (CH_3CH_2O); 50.8 ($COOCH_3$); 40.3 (C(4)); 31.7 (C(2')); 25.5 (C(5)); 18.7 (CH_3–C(3)); 15.1 (CH_3CH_2O), 14.0 (CH_3–C(7)). MS: 350 (1, M^+), 348 (1, M^+), 223 (8), 181 (21), 180 (23), 165 (28), *153* (100), *151* (100), 139 (21), 125 (76), 123 (80), 121 (93), 114 (22), 73 (32), 72 (26).

Cbl-Catalysed Electrolysis of **13**: *(±)-(3'*RS,*5'*RS,*2*E*)- and (±)-(3'*RS,*5'*SR,*2*E*)-Methyl 6-(5'-Ethoxy-3'-methyloxolan-3'-yl)-3-methylhex-2-enoate* (**18a** and **18a'**, resp.), *(±)-(3'*RS,*5'*RS,*2*E,*5*E*)-Methyl 6-(5'-Ethoxy-3'-methyloxolan-3'-yl)-3-methylhexa-2,5-dienoate* (**18b**), *and (±)-(3'*RS,*5'*RS*)- and (±)-(3'*RS,*5'*SR*)-Methyl 6-(5'-Ethoxy-3'-methyloxolan-3'-yl)-3-methylidenehexanoate* (**18c** and **18c'**, resp.). To the cathode compartement of an electrochemical cell (see *Fig.*), containing C-felt (*ca.* 0.7 g) as cathode material and 0.3M $LiClO_4$/DMF (70 ml) as solvent, was added vitamin B_{12a} (54 mg, 39 μmol, 3 mol-% with respect to **13**). The anode compartment was charged with 0.3M $LiClO_4$/DMF (7 ml). Vitamin B_{12} was reduced (under addition of a few drops of AcOH) to Co^I at −1.2 V (*vs.* SCE) until the current had dropped to a background level of *ca.* 2.4 mA and the colour had changed from red to black (dark green). Then, **13** (0.52 g, 1.49 mmol) was added by syringe, whereby the colour of the catholyte changed to red. Electrolysis was continued at −1.2 V under irradiation with a 500-W halogen lamp and

cooling to *ca.* 25°. The current of initially *ca.* 20 mA gradually dropped and reached, after 47 h, a background level of 1.2 mA. The reaction was followed by GC, and by end of the electrolysis, all **13** was consumed. The soln. was poured into ice/H_2O and extracted with Et_2O (5 × 50 ml). The org. soln. was washed with brine, dried ($NaSO_4$), and evaporated. The crude oil was purified by FC (Et_2O/pentane 1:6, silica gel): 0.35 g (87%) of **18**, R_f 0.33–0.40. Semi-prep. HPLC (*LiChrosorb Si 60* from *Merck*, 5 μm, 10 mm × 250 mm; hexane/(*t*-Bu)MeO 9:1, flow rate 5.7 ml/min; 7 × 10 μl, sample/solvent 2:1; detection at 220 nm) of **18** (50 mg) gave 25.8 mg (52% of **18**) of **18a**/**18a'**, 1.8 mg (4% of **18**) of **18b** and 17.7 mg (34% of **18**) of **18c**/**18c'**.

18a/**18a'** (*cis*/*trans* 15:1): $[\alpha]_D^{25} = 0.40 \pm 0.10$ (*c* = 0.99, hexane). GC (*SE-54*, 20 m, 100–250°, 5°/min): R_t 18.7 (**18a**) and 19.2 (**18a'**), besides 5% of unknown. Anal. GC (chiral phase): *ca.* 1:1 ratio for the enantiomers of both **18a** and **18a'**. ^{1}H-NMR (300 MHz, $CDCl_3$; data of the prevailing *cis*-epimer): 5.68–5.64 (*m*, H–C(2)); 5.17 (*X* of *ABX*, H–C(5')); 3.75, 3.44 (*AM* of AMX_3, $J_{AM} = 9.6$, $J_{AX} = J_{MX} = 7.1$, CH_3CH_2O); 3.69 (*s*, COOMe); 3.62, 3.48 (*AB*, $J_{AB} = 8.1$, $CH_2(2')$); 2.15 (*d*, $J = 1.3$, Me–C(3)); 2.14 (br. *t*, $J = 7.1$, $CH_2(4)$); 1.88, 1.65 (*AB* of *ABX*, $J_{AB} = 13.3$, $J_{AX} = 5.8$, $J_{BX} = 3.4$, $CH_2(4')$); 1.53–1.37 (*m*, $CH_2(5)$, $CH_2(6)$); 1.20 (*t*, $J = 7.1$, CH_3CH_2O); 1.04 (*s*, Me–C(3')). ^{13}C-NMR (75 MHz, $CDCl_3$; data of the prevailing *cis*-epimer): 167.2 ($COOCH_3$); 159.9 (C(3)); 115.4 (C(2)); 104.6 (C(5')); 77.6 (C(2')); 63.2 (CH_3CH_2O); 50.8 ($COOCH_3$); 46.1 (C(4')); 42.3 (C(3')); 41.4, 38.8 (C(4), C(6)); 24.9 (CH_3–C(3')); 23.3 (C(5)); 18.7 (CH_3–C(3)); 15.3 (CH_3CH_2O). GC/MS (*SE-54*; identical MS for **18a'** and **18a**): 241 (< 1), 224 (1), 193 (1), 192 (1), 147 (3), 121 (5), 114 (7), 95 (10), *83* (100), 67 (7), 55 (26), 43 (13), 41 (21).

18b: GC (*SE-54*, 20 m, 100–250°, 5°/min): 87% of **18b**, R_t 18.1. ^{1}H-NMR: 5.67–5.64 (*m*, H–C(2)); 5.66 (*td*, $J = 15.6, 1.2$, H–C(6)); 5.43 (*td*, $J = 15.6, 6.8$, H–C(5)); 5.21 (*X* of *ABX*, H–C(5')); 3.76, 3.46 (*AB* of ABX_3, $J_{AB} = 9.6$, $J_{AX} = J_{BX} = 7.1$, CH_3CH_2O); 3.76, 3.50 (*AB*, $J_{AB} = 8.5$, $CH_2(2')$); 3.69 (*s*, COOMe); 2.83 (*d*, $J = 6.8$, $CH_2(4)$); 2.14 (*d*, $J = 1.2$, Me–C(3)); 1.99, 1.82 (*AB* of *ABX*, $J_{AB} = 13.5$, $J_{AX} = 5.7$, $J_{BX} = 3.7$, $CH_2(4')$); 1.21 (*t*, $J = 7.1$, CH_3CH_2O); 1.18 (*s*, Me–C(3')). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.2 ($COOCH_3$); 158.8 (C(3)); 139.0 (C(6)); 123.9 (C(5)); 115.7 (C(2)); 104.7 (C(5')); 76.9 (C(2')); 63.3 (CH_3CH_2O); 50.9 ($COOCH_3$); 46.7 (C(4')); 44.6 (C(3')); 43.8 (C(4)); 24.5 (CH_3–C(3')); 18.8 (CH_3–C(3)); 15.3 (CH_3CH_2O). GC/MS (*SE-54*): 238 (1), 223 (1), 207 (7), 192 (12), 160 (13), 147 (33), 125 (53), *97* (100), 91 (42) 83 (69), 55 (82), 41 (79).

18c/**18c'** (*cis*/*trans* 12:1): GC (*SE-54*, 20 m, 100–250°, 5°/min); R_t 16.8 (**18c**) and 17.2 (**18c'**), besides 6% of unknown. ^{1}H-NMR (300 MHz, $CDCl_3$; data of the prevailing *cis*-epimer): 5.17 (*X* of *ABX*, H–C(5')); 4.93, 4.91 (2 br. *s*, CH_2=C(3)); 3.75, 3.44 (*AM* of AMX_3, $J_{AM} = 9.6$, $J_{AX} = J_{MX} = 7.1$, CH_3CH_2O); 3.69 (*s*, COOMe); 3.63, 3.49 (*AB*, $J_{AB} = 8.1$, $CH_2(2')$); 3.04 (br. *s*, $CH_2(2)$); 2.09 (br. s, $CH_2(4)$); 1.89, 1.66 (*AB* of *ABX*, $J_{AB} = 13.3$, $J_{AX} = 5.8$, $J_{BX} = 3.5$, $CH_2(4')$); 1.50–1.38 (*m*, $CH_2(5)$, $CH_2(6)$); 1.20 (*t*, $J = 7.1$, CH_3CH_2O); 1.04 (*s*, Me–C(3')). ^{13}C-NMR (75 MHz, $CDCl_3$; data of the prevailing *cis*-epimer): 171.9 ($COOCH_3$); 142.1 (C(3)); 113.7 (CH_2=C(3)); 104.6 (C(5')); 77.6 (C(2')); 63.1 (CH_3CH_2O); 51.8 ($COOCH_3$); 46.1 (C(4')); 42.3 (C(3')); 41.7, 38.7, 36.4 (C(2), C(4), C(6)); 24.9 (CH_3–C(3')); 23.2 (C(5)); 15.2 (CH_3CH_2O). GC/MS (*SE-54*; identical MS for **18c'** and **18c**): 241 (< 1), 225 (< 1), 209 (< 1), 194 (1.5), 180 (2), 147 (2), 133 (4), 121 (7), *83* (100), 55 (27), 41 (20).

4. *Synthesis and Cyclisations of (Bromomethyl)silyl Ethers. (*E*)-7-[(Bromomethyl)dimethylsilyloxy]-6-methylhepta-1,5-diene* (**14**). To a soln. of **1** (1.3 g, 10.3 mmol), $(CH_2Br)Me_2SiCl$ (1.4 ml, 10.3 mmol), and 4-(dimethylamino)pyridine (10 mg) in CH_2Cl_2 (15 ml) at 0°, Et_3N (1.5 ml, 10.7 mmol) was injected gradually within 30 min. The mixture was stirred at 0° for 3 h, and then pentane (20 ml) was added and the mixture filtered through *Celite*. The solvent was evaporated and the residue distilled in the 'Kugelrohr' (50–55°, 7×10^{-3} mbar): 2.59 g (90%) of **14**. Colourless oil. GC: dec. on heating block. IR (CCl_4): 3000–2900*s*, 2830*m*, 1470*m*, 1390*m*, 1365*m*, 1260*m*, 1235*m*, 1200*m*, 1080*m*, 1020*w*, 910*w*, 850*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.90–5.72 (*m*, H–C(2)); 5.46–5.38 (*m*, H–C(5)); 5.10–4.95 (*m*, $CH_2(1)$); 4.08 (*s*, $CH_2(7)$); 2.50 (*s*, $(CH_2Br)Si$); 2.16–2.10 (*m*, $CH_2(4)$, $CH_2(3)$); 1.65 (*s*, Me–C(6)); 0.28 (*s*, Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.4 (C(5)); 134.2 (C(6)); 125.4 (C(2)); 114.7 (C(1)); 69.2 (C(7)); 33.6, 27.1 (C(4), C(3)); 16.0 ($(CH_2Br)Si$); 13.6 (CH_3–C(6)); –3.1 ($(CH_3)_2Si$).

Radical Cyclisation of **14**: *(±)-(1*RS,*6*SR,*9*SR*)- and (±)-(1*RS,*6*SR,*9*RS*)-1,4,4,9-Tetramethyl-3-oxa-4-silabicyclo[4.3.0]nonane* (**19a** and **19b**, resp.). a) *Tin-Hydride Method*: A soln. of **14** (250 mg, 0.9 mmol) in benzene (50 ml) was heated to reflux. A soln. of 2,2'-azobis[isobutyronitrile] (AIBN; 10 mg) and Bu_3SnH (0.37 ml, 1.4 mmol) in benzene (10 ml) was injected by a mechanical syringe pump within 2 h, and the mixture was heated to reflux for an additional 2 h. The benzene was then removed *i.v.* and the residue purified by FC (Et_2O/pentane 1:50, 40 g silica gel). Chromatography yielded 150 mg (60%) of **14** with R_f 0.05 and 70 mg (37%) of **19a**/**19b** (ratio 1:2) with R_f 0.40.

19a: GC (*SE-54*, 20 m, 40–250°, 3°/min): R_t 20.8 (63% of **19**). GC/MS (*SE-54*): 198 (8, M^+), 184 (6), 183 (24), 166 (1), 155 (5), 141 (10), 127 (18), 115 (8), 108 (12), 99 (8), 89 (94, $CH_2Si(CH_3)_2OH^+$), *75* (100, $Si(CH_3)_2OH^+$), *59* (27), 43 (13), 41 (18), 39 (8).

19b: GC (*SE-54*, 40–250°, 3°/min): R_t 21.0 (31% of **19**). GC/MS (*SE-54*): 198 (8, M^+), 184 (5), 183 (25), 180 (3), 166 (4), 155 (6), 141 (13), 127 (12), 115 (6), 108 (18), *89* (100), 75 (94), 59 (24), 43 (14), 41 (16), 39 (8).

b) *Cbl-Catalysed Electrolysis*: To the cathode compartment of the electrochemical cell [12c], containing C-felt (1.5 g) as cathode material, was added vitamin B_{12a} (130 mg, 94 μmol, 12 mol-% with respect to **14**) in 0.2M $LiClO_4$/DMF (60 ml). The anode compartment was charged with 0.2M $LiClO_4$/DMF (10 ml). Vitamin B_{12a} was reduced to Co^I at a potential of −1.2 V (*vs.* SCE) until a stable background current of *ca.* 2.5 mA was observed. Then **14** (200 mg, 0.72 mmol) was added to the green soln. and the cell irradiated with a 250-W halogen lamp. A current of *ca.* 20 mA was observed. After 24 h, the current had diminished to a constant value of *ca.* 2 mA. The soln. was poured into brine (300 ml) and extracted with Et_2O (8 × 40 ml), the org. extract dried ($MgSO_4$) and evaporated, and the crude oil purified by FC (Et_2O/pentane 1:50, 10 g silica gel): 9.3 mg (6%) of **19a**/**19b** (ratio 2:1) and 82.0 mg (90%) of **1**. Spectroscopic data of **19a** were consistent with that of **19a** obtained by the tin-hydride method described above.

(±)-(1RS,2SR,5SR)- and (±)-(1RS,2SR,5RS)-1,5-Dimethylcyclopentane-1,2-dimethanol (**20a** and **20b**, resp.). To a soln. of **19a**/**19b** (obtained by the tin-hydride method; 70 mg, 0.35 mmol) in DMF (3 ml), KF (132 mg, 2.3 mmol) and 30% H_2O_2 soln. (0.27 ml, 2.4 mmol) were added and then heated at 60° for 7 h. After stirring at r.t. for additional 48 h, sat. Na_2SO_3/H_2O (0.5 ml) was added to destroy residual H_2O_2. The mixture was then diluted with brine (50 ml) and extracted with Et_2O (5 × 20 ml). The combined org. extracts were dried ($MgSO_4$) and the solvent removed *i.v.* The crude oil was purified by FC (Et_2O/pentane 3:2, 10 g silica gel): 42 mg (75%) of **20a**/**20b** (GC (*SE-54*, 20 m, 3°/min): ratio 1:2, R_t 27.7 and 28.2, resp.). Samples of the two compounds were obtained by prep. GC (5% *Carbowax 20 M* on *Chromosorb G-AW-DMCS*, 60–80 mesh, 1 × 43 cm, N_2, 0.6 bar, 140°).

20a (purity 90%): ^{1}H-NMR (300 MHz, $CDCl_3$): 3.85, 3.71 (*AB* of *ABX*, J_{AB} = 11.6, J_{AX} = 4.9, J_{BX} = 2.1, CH_2OH); 3.58, 3.38 (*AB*, J_{AB} = 11.2, CH_2OH); 2.91 (br. *s*, 2 OH); 1.86–1.61 (*m*, H–C(2), CH_2(3), H–C(5)); 1.37–1.25 (*m*, CH_2(4)); 1.03 (*s*, Me–C(1)); 0.89 (*d*, *J* = 7.0, Me–C(5)). NOE: Me–C(1)/H–C(2), 1 H of $HOCH_2$–C(1). ^{13}C-NMR (100 MHz, $CDCl_3$): 63.4 (CH_2OH); 62.0 (CH_2OH); 51.7 (C(2)); 45.5 (C(5)); 30.5 (C(3)); 23.7 (C(4)); 22.1 (CH_3–C(1)); 13.8 (CH_3–C(5)); C(1) too small to be detected. MS: 154 (1.5, $[M - 4H]^+$), 140 (1.5, $[M - H_2O]$), 127 (1.5), 125 (3), 110 (38), 109 (46), 99 (21), 96 (19), 95 (86), 93 (18), 82 (16), *81* (100, $C_6H_9^+$), 79 (18), 71 (14), 69 (25), 68 (26), 67 (70), 55 (56), 43 (50), 41 (61), 39 (34).

20b (purity 90%): ^{1}H-NMR (300 MHz, $CDCl_3$): 3.69, 3.58 (*AB* of *ABX*, J_{AB} = 11.3, J_{AX} = 9.1, J_{BX} = 3.5, CH_2OH); 3.58, 3.38 (*AB*, J_{AB} = 11.4, CH_2OH); 3.30 (br. *s*, 2 OH); 1.94–1.87 (*m*, H–C(2)); 1.82–1.65 (*m*, CH_2(3)); 1.64–1.53 (*m*, H–C(5)); 1.30–1.06 (*m*, CH_2(4)); 0.90 (*s*, Me–C(1)); 0.86 (*d*, *J* = 6.8, Me–C(5)). NOE: Me–C(1)/H–C(2), 1 H of $HOCH_2$–C(1), H–C(5); Me–C(5)/1 H of $HOCH_2$–C(1). ^{13}C-NMR (100 MHz, $CDCl_3$): 67.5 (CH_2OH); 64.4 (CH_2OH); 50.9 (C(2)); 46.5 (C(1)); 39.0 (C(5)); 31.6 (C(3)); 26.5 (C(4)); 20.2 (CH_3–C(1)); 14.6 (CH_3–C(5)). MS: 154 (1, $[M - 4H]^+$), 140 (0.3, $[M - H_2O]^+$), 127 (1), 126 (2), 125 (3), 110 (35), 109 (54), 99 (4), 96 (16), *95* (100, $C_7H_{11}^+$), 93 (10), 82 (10), 81 (78), 79 (15), 71 (10), 69 (25), 68 (25), 67 (76), 55 (52), 43 (36), 41 (58), 39 (25).

(2E,6E)-Methyl 8-[(Bromomethyl)dimethylsilyloxy]-3,7-dimethylocta-2,6-dienoate (**15**). To a soln. of **4** (382 mg, 1.93 mmol), $(CH_2Br)Me_2SiCl$ (0.26 ml, 1.9 mmol) and 4-(dimethylamino)pyridine (10 mg) in CH_2Cl_2 (10 ml) at 0°, Et_3N (0.35 ml, 2.5 mmol) was injected gradually within 30 min. The mixture was stirred at 0° for 3 h and then diluted with pentane (30 ml), filtered through *Celite*, and the solvent removed *i.v.*: 610 mg of **15** (90%). GC: dec. on heating block. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.62–5.61 (*m*, H–C(2)); 5.31–5.28 (*m*, H–C(6)); 3.99 (*s*, CH_2(8)); 3.62 (*s*, COOMe); 2.42 (*s*, $(CH_2Br)Si$); 2.17–2.12 (*m*, CH_2(4), CH_2(5)); 2.11 (*d*, *J* = 1.2, Me–C(3)); 1.57 (*s*, Me–C(7)); 0.21 (*s*, Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 167.1 (C(1)); 159.6 (C(3)); 134.9 (C(7)); 124.1 (C(2)); 115.5 (C(6)); 68.8 (C(8)); 50.7 ($COOCH_3$); 40.5 (C(4)); 25.5 (C(5)); 18.7, 13.5 (CH_3–C(3), CH_3–C(7)); 16.3 ($(CH_2Br)Si$); −3.1 ($(CH_3)_2Si$).

Radical Cyclisation of **15**: *(±)-(1RS,6SR,9SR)- and (±)-(1RS,6SR,9RS)-Methyl 1,4,4,9-Tetramethyl-3-oxa-4-silabicyclo[4.3.0]nonane-9-acetate* (**21a** and **21b**, resp.). a) *Tin-Hydride Method*: To a soln. of **15** (450 mg, 1.43 mmol) in benzene (50 ml) at reflux, a soln. of AIBN (10 mg) and Bu_3SnH (0.46 ml, 1.7 mmol) in benzene (10 ml) was injected by a mechanical syringe pump within 2 h, and the mixture was heated at 80° for an additional 2 h. The benzene was then removed *i.v.* and the oil obtained purified by FC (Et_2O/pentane 1:9, 10 g silica gel): 180 mg (64%) of **4** (R_f 0.05) and 118 mg (30%) of **21a**/**21b** (R_f 0.30 and 0.25, resp.) in ratio of *ca.* 1:1. For analysis, the compounds were separated by prep. GC (*SE-54*, 40–250°, 3°/min).

21a: GC: R_t 41.8, purity 95%. IR (CCl_4): 2960*m*, 2880*m*, 1740*s*, 1250*m*, 1060*m*, 860*m*, 840*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.65 (*s*, COOMe); 3.82, 3.44 (*AB*, J_{AB} = 11.4, CH_2(2)); 2.29, 2.20 (*AB*, J_{AB} = 13.4, CH_2COOMe); 2.20–2.09 (*m*, H–C(6)); 1.99–1.84, 1.61–1.46 (2*m*, CH_2(7), CH_2(8)); 0.99 (*s*, Me–C(1)); 0.95 (*s*, Me–C(9)); 0.84, 0.62 (*AB* of *ABX*, J_{AB} = 15.1, J_{AX} = 6.4, J_{BX} = 6.0, CH_2(5)); 0.19, 0.15 (2*s*, Me_2Si). NOE: Me–C(1)/H_β–C(2), H_β–C(5), H–C(6); H_α–C(2)/Me–C(9). ^{13}C-NMR (100 MHz, $CDCl_3$): 173.5 ($COOCH_3$); 66.0 (C(2)); 51.2

($COOCH_3$); 47.4, 46.0 (C(1), C(9)); 42.2 (C(6)); 42.2 (C(8)); 35.0 (C(7)); 30.8 (CH_2COOCH_3); 20.2, 18.9 (CH_3–C(1), CH_3–C(9)); 14.5 (C(5)); 0.4, −0.3 ($(CH_3)_2Si$). MS: 255 (0.4), 198 (2), 197 (15), 196 (10), 162 (5), 147 (5), 141 (16), 108 (10), 107 (13), 91 (18), *89* (100), 75 (40), 59 (36), 43 (17), 41 (18).

21b: GC: R_t 42.0, purity 96%. IR (CCl_4): 2960*m*, 2880*m*, 1740*s*, 1250*m*, 1055*m*, 910*s*, 860*m*, 840*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.64 (*s*, COOMe); 3.80, 3.42 (*AB*, J_{AB} = 11.4, CH_2(2)); 2.40–2.28 (*m*, H–C(6)); 2.20, 2.10 (*AB*, J_{AB} = 13.3, CH_2COOMe); 1.95–1.84, 1.68–1.54 (2*m*, CH_2(7), CH_2(8)); 0.99 (*s*, Me–C(1)); 0.95 (*s*, Me–C(9)); 0.86, 0.60 (*AB* of *ABX*, J_{AB} = 15.2, J_{AX} = 7.1, J_{BX} = 3.1, CH_2(5)); 0.21, 0.15 (2*s*, Me_2Si). NOE: Me–C(1)/H_β–C(2), H_β–C(5), H–C(6); H_α–C(2)/1 H of MeOOCCH_2–C(9). ^{13}C-NMR (100 MHz, $CDCl_3$): 173.2 ($COOCH_3$); 65.6 (C(2)); 51.2 ($COOCH_3$); 46.9, 45.1 (C(1), C(9)); 41.1 (C(8)); 41.1 (C(6)); 36.2 (C(7)); 29.2 (CH_2COOCH_3); 23.1, 16.8 (CH_3–C(9), CH_3–C(1)); 12.4 (C(5)); 0.6, 0.2 ($(CH_3)_2Si$). MS: 270 (1, M^+), 255 (3), 239 (1.5), 197 (20), 156 (6), 141 (34), 108 (10), 107 (18), 93 (15), 91 (22), *89* (100), 75 (52), 59 (37), 43 (15), 41 (17).

b) *Cbl-Catalysed Electrolysis*: The radical cyclisation of **15** (88 mg, 0.25 mmol) was performed in 0.2M $LiClO_4$/DMF (60 ml) in presence of vitamin B_{12a} (50 mg, 33 μmol, 13 mol-% with respect to **15**) in an electrochemical cell at −1.2 V (*vs.* SCE) as previously described. FC (Et_2O/pentane 1:9, 8 g silica gel) gave 45 mg of **4** (91%) and 5.0 mg (7%) of only **21a** (no **21b**). GC and ^{1}H-NMR (300 MHz) were consistent with that of **21a** obtained by the tin-hydride method described above.

*(2*E*,6*E*,10*E*)-Methyl 12-[(Bromomethyl)dimethylsilyloxy]-7,11-dimethyldodeca-2,6,10-trienoate* (**16**). To a soln. of **7b** (168 mg, 0.67 mmol), (CH_2Br)Me_2SiCl (90 μl, 0.67 mmol), and 4-(dimethylamino)pyridine (10 mg) in CH_2Cl_2 (5 ml) at 0°, Et_3N (92 μl, 0.67 mmol) was slowly added by syringe and the soln. stirred at 0° for 1.5 h. Pentane (20 ml) was then added, the mixture filtered through *Celite*, and the solvent evaporated: 250 mg (93%) of **16**. Colourless oil. TLC (Et_2O/pentane 1:9): only one spot, R_f 0.47. GC: dec. on heating block. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.97 (*td*, *J* = 15.7, 6.7, H–C(3)); 5.83 (*td*, *J* = 15.7, 1.5, H–C(2)); 5.40–5.35 (*m* (*t*-like), H–C(10)); 5.17–5.09 (*m* (*t*-like), H–C(6)); 4.05 (*s*, CH_2(12)); 3.72 (*s*, COOMe); 2.50 (*s*, (CH_2Br)Si); 2.30–2.00 (*m*, CH_2(4), CH_2(5), CH_2(8), CH_2(9)); 1.66, 1.61 (2*s*, Me–C(7), Me–C(11)); 0.25 (*s*, Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 167.1 (C(1)); 149.4 (C(3)); 136.1, 133.9 (C(7), C(11)); 125.8, 123.0, 121.0 (C(2), C(6), C(19)); 69.2 (C(12)); 51.4 ($COOCH_3$); 39.2 (C(8)); 32.4 (C(4)); 26.5, 26.1 (C(5), C(9)); 16.0 ((CH_2Br)Si); 16.0, 13.5 (CH_3–C(7), CH_3–C(11)); −3.1 ($(CH_3)_2Si$).

Radical Cyclisation of **16**: *Methyl 1,6,11,11-Tetramethyl-12-oxa-11-silatricyclo[7.4.0.0^{2,6}]tridecane-5-acetate* (**22**). A soln. of **16** (250 mg, 0.62 mmol) in benzene (20 ml) was heated to reflux. A soln. of AIBN (10 mg) and Bu_3SnH (0.21 ml, 0.8 mmol) in benzene (10 ml) was injected by a mechanical syringe pump within 2 h, and the soln. was refluxed for an additional 2 h. The benzene was removed *i.v.* and the residue purified initially by FC (Et_2O/pentane 1:9, 10 g silica gel) to give 4 fractions. *Fr. 1*: R_f 0.45, 25 mg (10%) of **16**, identified by TLC and ^{1}H-NMR; *Fr. 2*: R_f 0.30, 28 mg (14% calc. as $C_{18}H_{32}O_3Si$); *Fr. 3*: R_f 0.25–0.30, 28 mg (14% calc. as $C_{18}H_{32}O_3Si$); *Fr. 4*: R_f 0.05, 80 mg (51%) of **7b**, identified by TLC and ^{1}H-NMR. *Fr. 2* showed in GC (*SE-54*, 20 m, 100–250°, 3°/min) 2 peaks at R_t 37.6 and 38.2 (ratio *ca.* 2:1), *Fr. 3* many peaks between R_t 37.6 and 38.2, but mainly the same components as in *Fr. 2*. For spectroscopic analysis of compounds with R_t 37.6 and 38.2, *Fr. 2* was submitted twice to HPLC (*LiChrosorb Si60* from *Merck*, (*t*-Bu)EtO/hexane 1:9, detection at 206 nm) affording 2.5 mg of **22a** (GC: R_t 37.6, purity 83%) and 1.0 mg of **22b** (GC: R_t 38.2, purity 77%).

22a: ^{1}H-NMR (400 MHz, $CDCl_3$): 3.66 (*s*, COOMe); 3.53, 3.34 (*AB*, *J* = 10.7, CH_2(13)); 2.46–2.36 (*m*, 1 H, MeOOCCH_2–C(5)); 2.12–1.97 (*m*, H–C(5), H–C(4), 1 H of MeOOCCH_2–C(5)); 1.58–1.31 (*m*, H–C(9), CH_2(8), H_{eq}–C(7), CH_2(3)); 1.28–1.01 (*m*, H–C(2), H_{ax}–C(7), H–C(4)); 0.95 (*s*, Me–C(6)); 0.89 (*s*, Me–C(1)); 0.56 (*t*, *A* of *ABX*, J_{AB} = 14.4, J_{AX} = 13.5, H_{ax}–C(10)); 0.37 (*dd*, *B* of *ABX*, J_{AB} = 14.4, J_{BX} = 3.1, H_{eq}–C(10)); 0.16 (*s*, Me_{eq}–C(11)); 0.13 (*s*, Me_{ax}–C(11)). NOE: Me–C(1)/Me–C(6), H_{ax}–C(10), H_{eq}–C(13); H_{ax}–C(2)/1 H of MeOOCCH_2–C(5), H_{ax}–C(9), H_{ax}–C(13); Me–C(6)/H_{ax}–C(8). ^{13}C-NMR (75 MHz, $CDCl_3$): 174.2 ($COOCH_3$); 75.4 (C(13)); 51.5 ($COOCH_3$); 49.9 (C(2)); 45.6 (C(5)); 43.8 (C(6)); 43.3 (C(9)); 39.6 (C(1)); 37.8 (CH_2COOCH_3); 34.4 (C(7)); 31.4 (C(8)); 27.8 (C(4)); 23.1 (CH_3–C(6)); 21.2 (C(3)); 16.7 (C(10)); 11.2 (CH_3–C(1)); −0.4 ($CH_{3(eq)}$–C(11)); −2.4 ($CH_{3(ax)}$–C(11)). MS: 324 (4, M^+), 309 (1.5), 292 (2), 277 (2), 235 (1.5), 189 (6), 175 (7), 161 (16), 160 (14), 147 (20), 121 (22), 107 (24), 95 (11), 93 (19), 91 (25), *89* (100), 81 (23), 75 (60), 67 (15), 59 (52), 55 (25), 41 (27).

22b: ^{1}H-NMR (400 MHz, $CDCl_3$): 3.65 (*s*, COOMe); 3.50, 3.33 (*AB*, *J* = 10.7, CH_2–C(13)); 2.35–2.29 (*m*, 1 H, MeOOCCH_2–C(5)); 2.22–2.02 (*m*, 1 H, MeOOCCH_2–C(5)); 1.94–1.85 (*m*, H–C(4)); 1.80–1.69 (*m*, H–C(5)); 1.60–1.54 (*m*, H_{eq}–C(7)); 1.52–1.22 (*m*, H–C(9), CH_2(8), CH_2(3)); 1.18–1.04 (*m*, H–C(2), H_{ax}–C(7)); 0.90 (*s*, Me–C(1)); 0.72 (*s*, Me–C(6)); 0.56 (*t*, *A* of *ABX*, J_{AB} = 14.4, J_{AX} = 13.0, H_{ax}–C(10)); 0.38 (*dd*, *B* of *ABX*, J_{AB} = 14.4, J_{BX} = 2.8, H_{eq}–C(10)); 0.16 (*s*, Me_{eq}–Si); 0.12 (*s*, Me_{ax}–Si). NOE: Me–C(1)/Me–C(6), H_{ax}–C(10), H_{eq}–C(13); H_{ax}–C(2)/H–C(5), H_{ax}–C(9), H_{ax}–C(13); Me–C(6)/H_{ax}–C(8). ^{13}C-NMR (75 MHz, $CDCl_3$): 174.2 ($COOCH_3$); 75.1 (C(13)); 54.9 (C(2)); 51.4 ($COOCH_3$); 47.8 (C(5)); 43.5 (C(9)); 42.9 (C(1)); 39.9 (C(6)); 38.1

(C(7)); 34.9 (CH_2COOCH_3); 31.3 (C(8)); 28.1 (C(4)); 20.3 (C(3)); 16.7 (C(10)); 13.9 (CH_3–C(6)); 11.1 (CH_3–C(1)); −0.4 ($CH_{3(ax)}$–C(11)); −2.4 ($CH_{3(eq)}$–C(11)). MS: 324 (10, M^+), 309 (3), 293 (2), 292 (2), 277 (1), 235 (2), 204 (3.5), 189 (6), 161 (17), 160 (20), 147 (18), 121 (22), 107 (20), 95 (11), 93 (18), 91 (21), *89* (100), 81 (18), 75 (52), 67 (13), 59 (47), 55 (25), 41 (27).

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