193. 3-Triethylsilyloxypentadienyllithium, a Versatile 1,3-Diene- or Vinyl ketone-Building Block

by **Wolfgang Oppolzer, Roger L. Snowden** and **Dana P. Simmons**

Département de Chimie Organique, Université de Genève, CH-1211 Genève

Dedicated to Prof. *Vladimir Prelog* on the occasion of his 75th birthday

(24. VIII. 81)

Summary

Deprotonation of the 3-trialkylsilyloxy-1,4-diene **3a** and subsequent electrophilic substitution of the non-isolated 3-trialkylsilyloxypentadienyllithium **4** gives the α- and γ-products **8** and/or **6** in good yields. Whereas alkylation of **4** proceeds with variable regioselectivity *(Table 1)* aldehydes and ketones attack preferentially the γ-position of **4** *(Table 2)*. The desired γ-products **6** may be directly subjected to inter- and intramolecular [4 + 2]-additions as demonstrated by the reactions **5a** (≡ **6d**) → **7** and **6h** → **19** *(Schemes 4* and *12)*. Alternatively, smooth fluoride-promoted silylether-cleavage **6** → **11** *(Scheme 8)* provides a convenient approach to substituted vinyl ketones such as to the natural product **11f** *(Table 3)*. The stereoselective conversion **6k** → **23** *(Scheme 13)* implies an *endo*-selective intramolecular *Diels-Alder* addition (**26** → **23**) and exemplifies the use of **4** as an equivalent of the hypothetical anion **IV**. Furthermore, some electrophilic substitutions of the hexadienyllithium **15** have been studied *(Scheme 10)*.

Introduction. – The utility of intramolecular *Diels-Alder* reactions of type **A** → **B** *(Scheme 1)* in organic synthesis is well established [1]. Its exploitation for the efficient preparation of fused carbocyclic systems of type **B** requires particularly convergent C,C-bond formation to be provided by the polyene substrates **A**. In this context we reported recently in a preliminary note that the pentadienyl anions of type **I** present a convenient C_5-unit for both the construction and attachment of the functionalized dienes **II** and dienophiles **III** *(Scheme 2)*[2]. At the outset of our work it was known that metalated unsubstituted allyl ethers **2** (R′ = H) react with electrophiles in the γ- as well as in the α-position whereas metalation of the substituted ethers **1** (R′ = alkyl) is extremely slow [3] [4] *(Scheme 3)*. In contrast, 3-trialkylsilyloxy-1,4-pentadienes are smoothly deprotonated to form the symmetrical pentadienyllithium derivatives **I** which may be substituted by a variety of electrophiles. It is the purpose of this work to present these and related studies in full experimental detail.

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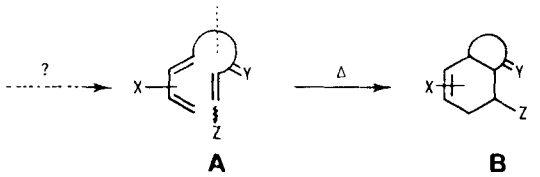
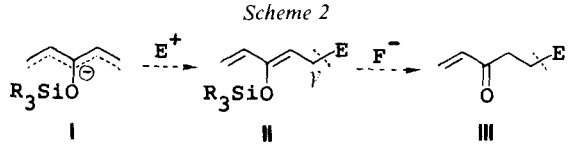
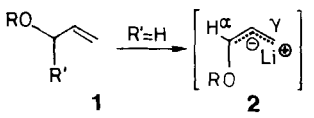
Scheme 1



Scheme 2

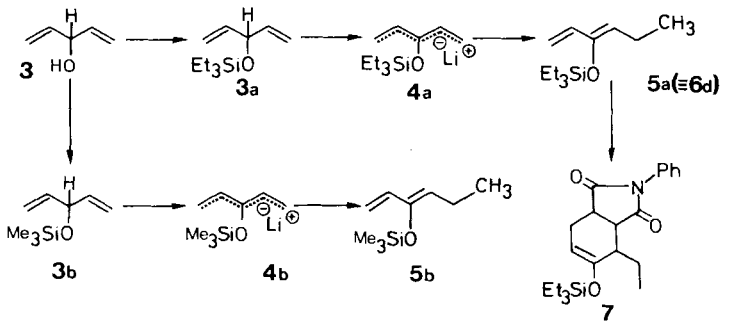


Scheme 3



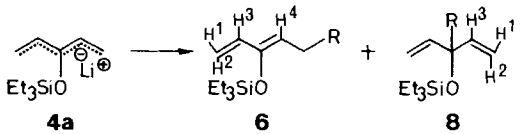
Preparation and electrophilic substitutions of 3-triethylsilyloxy-pentadienyllithium 4a *(Schemes 4, 5* and *6).* – The triethylsilylether **3a**, readily prepared [5] from the 1,4-pentadien-3-ol (**3**) [6], when treated with *sec*-butyllithium in THF at –78° followed by addition of methyliodide, furnished, regio- and stereoselectively, the γ-substituted silyloxydiene **5a**(≡**6d**) *(Scheme 4).* The *(3Z)*-configuration of **5a** (and therefore the depicted *W*-configuration of **4a** follows from a smooth bimolecular cycloaddition (proceeding between 25° and 80°) to *N*-phenyl-maleimide giving the adduct **7**. Similarly, silylation of **3** with *N*-(trimethylsilyl)acetamide [7] in refluxing pentane furnished the silyloxydiene derivative **3b** (76% yield) which was used immediately or stored at –30°. Analogous deprotonation and methylation of **3b** gave the diene **5b** in 85% yield. Since both the starting methylether **3b** and the alkylation product **5b** were less stable than the corresponding ethyl derivatives **3a** and **5a** the following studies focused on the latter which withstand chromatography on silica gel.

Scheme 4



Electrophilic substitutions of **4a** were investigated systematically particular attention being paid to their site-selectivity *(Scheme 5)*.

Scheme 5



4a **6** **8**

As shown in *Table 1* protonation with water and silylation with chlorotrialkylsilanes occur exclusively in the γ-position to furnish the products **6a–6c**.

Table 1. *Protonation and alkylation products of 3-triethylsilyloxypentadienyllithium* (**4a**) *and corresponding yields*

Electrophile		Products				
		R′ in **6** and **8**	Total Yield (**6**+**8**)%[a]	Rel.% of **6** (γ-product)	Rel.% of **8** (α-product)	Determined by
H_2O	**a**	H-	87	100	–	GC., ^{1}H-NMR.
Me_3SiCl	**b**	$(CH_3)_3Si$-	89	100	–	GC., ^{1}H-NMR.
Et_3SiCl	**c**	$(C_2H_5)_3Si$-	87	100	–	GC., ^{1}H-NMR.
CH_3I	**d**	CH_3-	85	100	–	GC., ^{1}H-NMR.
C_2H_5I	**e**	C_2H_5-	82	73	27	GC., ^{1}H-NMR.
n-$C_6H_{13}I$	**f**	n-C_6H_{13}-	82	50	50	GC.
i-C_3H_7I	**g**	i-C_3H_7-	85	23	77	GC.
$CH_2=CH(CH_2)_2Br$	**h**	$CH_2=CH(CH_2)_2$-	80	61	39	GC., ^{1}H-NMR.
$CH_2=CH(CH_2)_2OTs$	**h**	$CH_2=CH(CH_2)_2$-	78	9	91	GC.
$CH_2=CH(CH_2)_2OSO_2CF_3$	**h**	$CH_2=CH(CH_2)_2$-	71	2	98	GC.
$CH_2=CH$-CH_2Br	**i**	$CH_2=CHCH_2$-	77	67	33	GC., ^{1}H-NMR.
$(CH_3)_2C=CH$-CH_2Br	**j**	$(CH_3)_2C=CH$-CH_2-	76	92	8	GC.
$CH_2=CH$-$CH=CH$-CH_2Br	**k**	$CH_2=CH$-$CH=CH$-CH_2	76	75	25	GC., ^{1}H-NMR.
C_6H_5-CH_2Cl	**l**	C_6H_5-CH_2-	84	49	51	GC., ^{1}H-NMR.
Oxirane	**m**	OH-CH_2-CH_2-	87	41	59	GC., ^{1}H-NMR.

[a]) Yields are based on 3-triethylsilyloxy-1,4-pentadiene (**3a**).

Alkylation of **4a** afforded, generally in good yields, the desired γ-products **6** together with the α-products **8**. Thus, γ-, rather than α-attack is more or less preferred with primary alkyl and alkenyl halides (except hexyl iodide), whereas benzyl chloride and isopropyl iodide gave a product ratio **6l**/**8l** = 1:1 and **6g**/**8g** 1:3.3, respectively. The nature of the leaving group may also influence the regioselectivity. Thus, with electrophiles such as 3-butenyl *p*-toluenesulfonate and 3-butenyl trifluoromethanesulfonate α-substitution becomes increasingly important: in the last case the α-product **8h** is formed almost exclusively, whereas with oxirane the α-product **8m** is only slightly favored[1]) On the other hand, neither introduction of HMPA or TMEDA, nor exchange of the counterion by Zn^{++} or by K^+ significantly altered the γ/α-ratio in the alkylation of **4a** with 4-bromo-1-butene leading to **6h**/**8h**.

In contrast, dropwise addition of aldehydes or ketones to **4a** at –78°, and immediate quenching of the reaction mixture with aq. NH_4Cl-solution at –78° furnished after work-up the desired γ-products **6** mostly with high selectivity as depicted in

[1]) This trend, observed independently on alkylation reactions of phenyl-substituted allylanions [8], agrees with the concept of hard and soft acids and bases [9]; see also [10].

Table 2. Evidence for a kinetic control of the observed regioselectivity was provided by the non-interconvertibility of the isolated isomers **6q** and **8q** on treatment with *sec*-butyllithium or lithium hexamethyldisilazane in THF at –78° for 1 h. Condensation of an excess of formaldehyde into a 2M solution of **4a** in THF at –78° and subsequent warming-up of the reaction mixture to 0° gave the γ-product **6n** with 83 to 75% regioselectivity. Even at this relatively high temperature the ratio **6n**/**8n** is kinetically controlled; in fact neither **6n** nor **8n** were interconverted on deprotonation with *sec*-butyllithium at –78° and subsequent stirring with an excess of formaldehyde at 0° for 3 h.

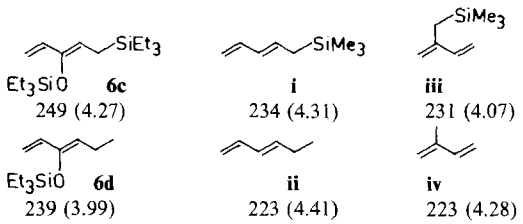
Table 2. *Reaction products of aldehydes and ketones with 3-triethylsilyloxypentadienyllithium* (**4a**) *and corresponding yields*

Electrophile		Products			
		R in **6** and **8**	Total Yield (**6**+**8**) %[a])	Rel.% of **6**[a]) (γ-product)	Rel.% of **8**[a]) (α-product)
$CH_2=O$	**n**	$CH_2(OH)$-	84	{83[b]) 75	{17[b]) 25
$CH_3CH=O$	**o**	$CH_3CH(OH)$-	90	97	3
$C_2H_5CH=O$	**p**	$C_2H_5CH(OH)$-	91	85	15
n-$C_3H_7CH=O$	**q**	*n*-$C_3H_7CH(OH)$-	85	82	18
$C_6H_5CH=O$	**r**	$C_6H_5CH(OH)$-	80	92	8
$(CH_3)_2C=O$	**s**	$(CH_3)_2C(OH)$-	85	97	3
Cyclohexanone	**t**	1-hydroxycyclohexyl	77	96	4
$(C_6H_5)_2C=O$	**u**	$(C_6H_5)_2C(OH)$-	89	100	–

[a]) Determined by isolation of **6** and **8**.
[b]) Determined by ^{1}H-NMR. analysis.

The structures of the separated isomers **6** and **8** were readily assigned by ^{1}H-NMR.evidence. Hence, the four different olefinic protons of the 1,3-dienes appear approximately at $\delta=4.8$ ppm (*t*, $J=7$, H^4); 5.0 ppm (*d*× *d*, $J=10$ and 2, H^1); 5.3 ppm (*d*× *d*, $J=17$ and 2, H^2) and 6.2 ppm (*d*× d, J = 17 and 10, H^3) (see *Scheme 5*). The symmetric isomers **8** exhibit three signals corresponding to 6 olefinic protons at $\delta=5.1$ ppm (*d*× *d*, $J=10$ and 2 H^1); 5.3 ppm (*d*× *d*, $J=17$ and 2, H^2) and 6.0 ppm (*d*× *d*, $J=17$ and 10, H^3) (see *Scheme 5*). Furthermore, the UV.spectra of the γ-products **6f**, **6g**, **6m**, **6n**, **6q**, **6r** and **6t** consistently show a maximum at 238–239.5 nm ($\log\varepsilon=4.1$–4.24). It is interesting to note that the *C*-silylated diene **6c** exhibits a UV.maximum at 249 nm ($\log\varepsilon=4.27$)[2]).

[2]) This bathochromic shift is most readily explained by hyperconjugation of the C,Si-bond with the diene system in **6c**. Further examination shows a similar difference in UV.absorbance between the dienes **i** [11] and **ii** [12], as well as, between the dienes **iii** [13] and **iv** [14] (hydrocarbon solvents, λ_{max} in nm ($\log\varepsilon$)). Analogous orbital overlap of a C,Si-bond with a π-system explains the UV., of trimethylbenzylsilane (λ_{max}221) as compared to 1-phenyl-2,2-dimethylpropane (λ_{max}211) [15].

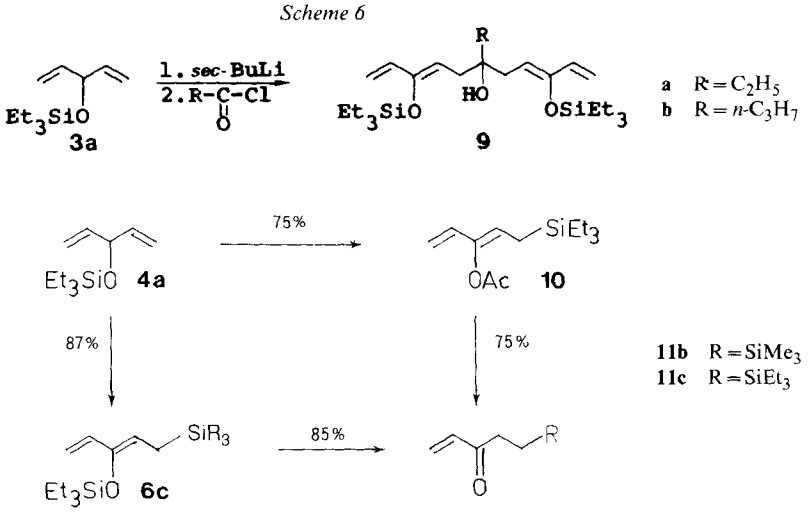


6c 249 (4.27) **i** 234 (4.31) **iii** 231 (4.07)

6d 239 (3.99) **ii** 223 (4.41) **iv** 223 (4.28)

Acylation of **4a** proved to be more complex than previously reported. Dropwise addition of a solution of freshly prepared **4a** in THF to an excess of propionyl- or butyryl chloride at –78°, followed by immediate quenching of the reaction mixture with aq. $NaHCO_3$-solution at –78°, furnished mainly the symmetrical 6-hydroxy-1,3,8,10-undecatetraenederivatives **9a** and **9b** in yields of 43 and 62%, respectively *(Scheme 6)*. The major formation of **9a** and **9b** in the presence of an excess of acyl chloride indicates a preferential γ-acylation of **4a** followed by an even faster reaction of the non-isolable ketone with a second molecule of **4a**. Under identical acylation conditions which led to the conversion **4a** → **9** but using acetyl chloride, the 3-triethylsilyl-1-vinyl-1-propenyl acetate (**10**) was obtained in 75% yield *(Scheme 7)*. The structure of **10** which implies an anionic [1,4]-Si-shift[3]) during the acylation process agrees with its spectral data (*e. g.* an IR.-band at 1765 cm^{-1}) and with its conversion to the triethylsilylpentenone **11c** (75% yield) by enol ester cleavage with methyllithium (2.5 mol-equiv.) in DME at –78° and quenching with aq. NH_4Cl-solution. Alternatively, the triethylsilylpentenone **11c** was obtained by silyl-ether cleavage of **6c** with KF/MeOH as described below. The fact that an analogous Si-migration during silylation of **4a** does not take place was established by analogous treatment of **6b** with KF/MeOH giving the trimethylsilylpentenone **11b** (90% yield).

Scheme 6



Conversion of the γ-products to the vinyl ketones 11. – A particular feature of the *O*-silyl-protecting group is its removal under mild non-acidic conditions [18]. In fact, smooth cleavage of the substituted silyloxydienes **6** with KF (1.5 mol-equiv.) in methanol at –10 to –5° furnished the functionalized vinyl ketones **11** in high yields *(Scheme 8, Table 3)*[4]). Thus, the undecenone **11f**, isolated from odoriferous seaweeds *Dictyopteris* [20] was readily prepared.

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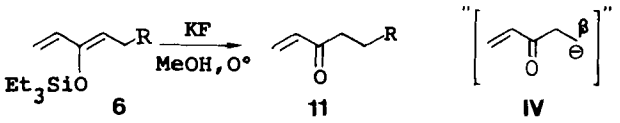
[3]) Analogous Si-migration (O → C) was observed on *O*-silylation of lithiated allyloxysilanes with chlorosilanes [16] [17].

[4]) The selective cleavage of a silyloxydiene under these non-acidic conditions was essential for a recent synthesis of norpatchoulenol [19].

Scheme 8



6 **11** **IV**

Table 3. *Conversion products of the silyloxydienes* **6** *to the vinyl ketones* **11** *(Scheme 8) and corresponding yields.*

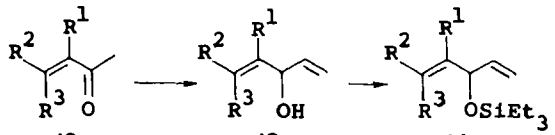
R in **11**		Method[a])	yield of **11** (%)
b	$(CH_3)_3Si$	A	90
c	$(C_2H_5)_3Si$	A	85
f	n-C_6H_{13}	A	78
j	$(CH_3)_2C=CHCH_2$	A	74
j	$(CH_3)_2C=CHCH_2$	B	70
o	$CH_3CH(OH)$	A	80

[a]) A: KF/MeOH, –10°–0°; B: KF/*i*-PrOH, +25°

At higher temperatures methyl ethers, derived from *Michael* addition of methanol to **11**, can be formed as shown by treatment of **6l** with KF/methanol at +15°. Alternatively, removal of the silyl group with KF (1.5 mol-equiv.) in 2-propanol may be carried out safely at room temperature as illustrated by the conversion **6j** → **11j**. It is worth mentioning that the inexpensive trimethylsilyl ether **4b**, may be carried through the deprotonation/substitution/ether-cleavage sequence without the isolation of intermediates to give the enones **III** in good yields [19b]. Consequently, the pentadienyllithium derivatives **I** represent convenient equivalents of the homoenolate anion of ethyl vinyl ketone.

We then attempted to extend the scope of this method by starting from the more substituted 3-silyloxy-1,4-dienes **14**. Some representative dienes **14** were readily prepared by the route **12** → **13** → **14** *(Scheme 9)*.

Scheme 9



12 **13** **14**

a $R^1=R^3=H$, $R^2=Me$
b $R^1=Me$, $R^2=R^3=H$
c $R^1=H$, $R^2=R^3=Me$
d R^1, $R^2=-(CH_2)_4-$, $R^3=H$

However, among these only **14a** could be deprotonated under sufficiently mild conditions to give the anion **15** *(Scheme 10)*. Due to the unsymmetrical nature of **15** electrophilic attack not only at the α-site but also in both the positions γ and γ' is possible. Reaction of **15** with some 'γ-selective' electrophiles *(Table 4)* gave the following results: γ-methylation with CH_3I occurred almost exclusively at the less substituted terminal, giving **16b** whilst reaction with H_2O and benzaldehyde furnished with decreasing selectivity mixtures of **16** and **17**. The depicted configuration of **16b** (and of the anion **15**) follows from its ^{1}H-NMR.spectrum which shows signals for three different olefinic protons at $\delta=4.62$ ppm (H^3), 5.7 ppm (H^1), and 5.9 ppm (H^2), ($J(H^1/H^2)=17$ Hz).

Scheme 10

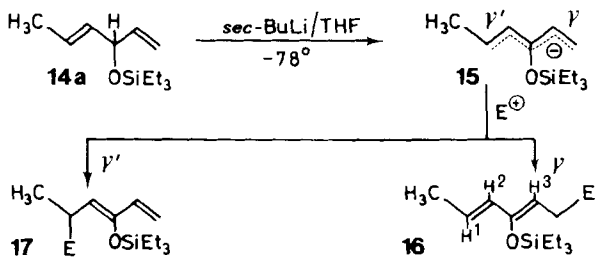


Table 4. *Electrophilic substitution products of the triethylsilyloxyhexadienyllithium* (**15**) *and corresponding yields.*

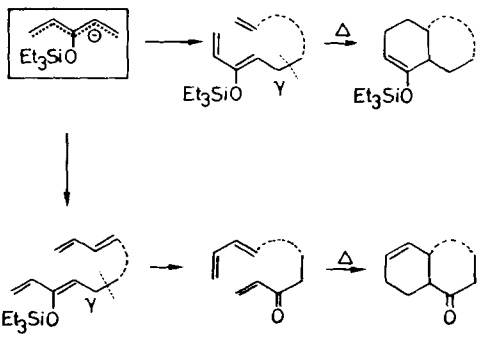
Electrophile		E in **16** and **17**	Total yield%[a]) (**16** + **17**)	Rel.% **16**[a])	Rel.% **17**[a])
H_2O	**a**	H	96	80	20
CH_3I	**b**	CH_3	95	97	–
C_6H_5CHO	**c**	$C_6H_5CH(OH)$	97	60[b])	40[b])

[a]) The products **17** and/or **16** were separated; the ratio **17**/**16** was determined by GC. and ^{1}H-NMR.-analysis of the crude reaction mixture; yields are based on the 1,4-diene **14a**.

[b]) Inseparable mixture, analysed by 250-MHz-^{1}H-NMR. spectroscopy.

Intramolecular [4 + 2]-cycloaddition reactions. – The feasibility of **4a** to serve as a masked, functionalizable diene as well as the dienophile unit in intramolecular *Diels-Alder* reactions is illustrated in *Scheme 11*.

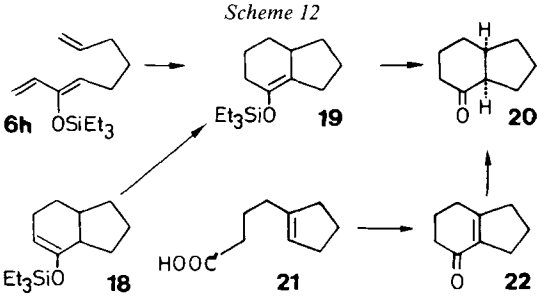
Scheme 11



Heating a 1.2%-solution of the triene **6h** in toluene at 160° for 17 h using a silylated, sealed pyrex tube furnished the bicyclic silyloxy compound **19** in 84% yield *(Scheme 12)*. Under these conditions the olefinic bond of the initally formed cycloadduct **18** must have shifted to the more stable position. Cleavage of **19** with KF/MeOH at –5 to + 5° gave the *cis*-fused bicyclononanone **20** in 81% yield. Kinetic deprotonation (LDA, THF, –78°) of **20** and subsequent *O*-silylation with chloro-

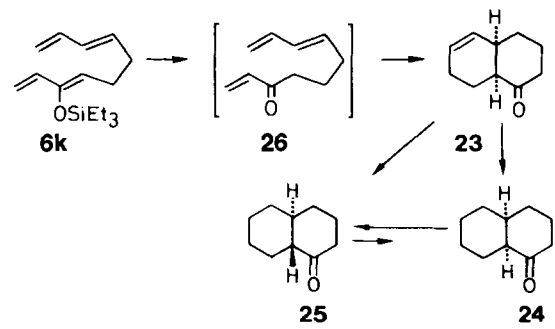
triethylsilane afforded the enol ether **18** (65% yield) which isomerized completely at 170° (17 h) to the more substituted enol ether **19** (82% yield). An independent 9-step approach to the indanone **20** involved the *Friedel-Crafts*-cyclization/hydrogenation sequence **21** [21] → **22** → **20**.

Scheme 12



The alternative use of **4a** as an equivalent of **IV** in intramolecular *Diels-Alder* reactions was demonstrated by cleavage of the silyloxytetraene **6k** with KF in methanol at –10° to 0° for 1 h. Subsequent work-up and chromatography furnished directly the *cis*-fused octahydronaphthalenone **23** as the sole adduct in 78% yield *(Scheme 13)*. Evidently, the initially formed ketone **26** undergoes an exceedingly smooth and stereoselective intramolecular [4+2]-addition to the diene unit. The mild reaction conditions, coupled with the observation that no deuterium was found in **23** after cleavage of **6k** in CD_3OD are in accord with a kinetically controlled *Diels-Alder* process which favors an *endo*-orientation of the carbonyl group in the transition state[5]). This stereochemical assignment of the adduct **23** is opposite to our previous one [2] which was based on the hydrogenation of **23** with Pd/C in abs. EtOH leading to the *trans*-bicyclo[4.4.0]decan-2-one) (**25**) (83%). The misleading epimerization which accompanies the hydrogenation **23** → **25** could be avoided by hydrogenation of **23** using *Wilkinson*'s catalyst [23] to give cleanly *cis*-bicyclo[4.4.0]decan-2-one (**24**), identified by comparison (GC., ^{13}C-NMR.) with an authentic sample prepared as described in [24]. Successive treatment of the cycloaduct **23** with $NaBH_4$, H_2/Pd/EtOH and CrO_3/pyridine also furnished pure *cis*-**24**.

Scheme 13



[5]) For an independent alternative preparation of **26** and its cycloaddition to give **23** see [22].

The useful applicability of this work has been exemplified by the syntheses of a strained bicyclo[4.3.1]decenone [25], of the sesquiterpenes norpatchoulenol [19], 3-methyl-5-(2,3,6-trimethylphenyl)-1-penten-3-ol [26], α-himachalene [27] and by closely related approaches to selena-3,7-diene [28] and epizonarene [29]. A reliable approach for the highly regioselective γ-alkylation of 3-silyloxydienyl anions is reported in the subsequent paper.

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Experimental Part

General. The normality of the *sec*-BuLi, commercially available *(Fluka)* in a cyclohexane solution, was determined immediately prior to its use by *Gilman*'s double titration method [30]. The same titration method was also used for determining the BuLi normality, available in a hexane solution *(Merck).*

Solvents and reagents were dried and purified prior to their use. Work-up refers to the general procedure of washing an organic phase with H_2O, sat. aq. $NaHCO_3$-, and then sat. aq. NaCl-solution, followed by drying over anhydrous Na_2SO_4, filtration, and removal of solvent by distillation *in vacuo (i. v.).*

All products were checked for purity by gas-liquid chromatography (GC.) or thin layer chromatography (TLC.). GC. was carried out on a *Carlo Erba SS455* with a 1m column of 5% OV225 on *Chromosorb* WAW 80/160 at a pressure of 1 kg/cm^2, retention time in min. For TLC. glass plates coated with Kieselgel 60F–254 were eluted with the solvent mixtures mentioned in the text and viewed under UV. light and developed with iodine. Column chromatography was carried out using SiO_2 *(Merck,* Art. 7734) Kieselgel 60 Korngrösse 0.063 → 0.2 mm, 70–230 mesh ASTM]; p.p refers to a column chromatography carried out using *ca.* 1 g of adsorbent packed in a *Pasteur* pipette. All solvents were distilled prior to their use for chromatographic purposes. Melting points were determined on a *Kofler* hot stage using polarized light and are uncorrected. Temperatures are expressed as degrees *Celsius.* – IR. spectra: in CCl_4 unless otherwise specified, $\tilde{\nu}_{max}$ in cm^{-1}. – UV. spectra: in cyclohexane unless otherwise specified, λ_{max} in nm ($\log\varepsilon$). – ^{1}H-NMR. spectra: at 100 MHz in $CDCl_3$, standard tetramethylsilane δ (ppm) = 0; abbreviations: *s* = singlet, *d* = doublet, *t* = triplet, *qa* = quadruplet, *qi* = quintet, *m* = multiplet, *J* = spin-spin coupling constant (Hz). – Mass spectra (MS.): signals are given in m/z (rel. %); high-resolution-MS. (HR.) were obtained using a *Varian SM 1* instrument.

3-Triethylsilyloxy-1,4-pentadiene (**3a**). Chlorotriethylsilane (19.1 g, 0.126 mol) was added dropwise to a stirred solution of 1.4-pentadien-3-ol (**3**) [7] (9.60 g, 0.114 mol) and imidazole (9.32 g, 0.137 mol) in dry DMF (10 ml) at 5°, under Ar. Then the reaction mixture was allowed to attain 25° during 1 h, left for a further 15 h at 25°, and then was poured into cold water. Extraction (pentane), work-up, and fractional distillation *i. v.* gave **3a** as a colorless oil (19.6 g, 88%), b.p. 72–74° (12 Torr). – Rf: 0.15 (pentane), 0.6 (benzene), GC. (108°): 4.56. – IR.: 2970, 2890, 1240, 1130, 930, 840. – ^{1}H-NMR.: 0.4–0.8 (6H); 0.8.–1.2 (9H); 4.63 (br. *t*, *J* = 5, 1H); 5.0–5.4 (4H); 5.86 (*d* × *d* × *d*, *J* = 17, 10 and 6, 2H). – MS.: ($M^{+\cdot}$ not observed), 170 (16), 169 (100), 141 (13), 113 (15), 103 (53).

3-Trimethylsilyloxy-1,4-pentadiene (**3b**). A solution of 1,4-pentadien-3-ol (**3**) [7] (2.6 g, 0.031 mol) and trimethylsilylacetamide (TMSA, 4.85 g, 0.037 mol) in dry pentane (20 ml) was refluxed during 1 h. The mixture was allowed to cool to 25° during 2 h and then kept at 0° for further 24 h. The reaction mixture was filtered and the solid was washed with cold pentane (10 ml). Concentration of the filtrate gave a colorless oil which was rapidly filtered through a small quantity of silica gel (to remove any excess of acetamide). Fractional distillation of the eluate afforded **3b**, oil (3.6 g, 76%), b.p. 99–101°/760 Torr, Rf (benzene) 0.65. – IR.: 2970, 1255, 1125, 990, 930. – ^{1}H-NMR.: 0.13 (*s*, 9H); 4.62 (br. *t*, *J* = 5, IH); 5.0–5.4 (4H); 5.86 (*d* × *d* × *d*, *J* = 17, 10 and 6, 2H). – MS.: 156 (19, $C_8H_{16}OSi^+$), 155 (38), 147 (81), 141 (100), 129 (24); HR.: M^+: Found 156.09696; Calc. 156.097038. The diene **3b** was stored at –30°.

(*Z*)-*3-Trimethylsilyloxy-1,3-hexadiene* (**5b**). A solution of *sec*-BuLi in cyclohexane (2 mmol) was added dropwise to a stirred solution of the **3b** (312 mg, 2 mmol) in dry THF (6 ml) at –78°, under Ar. After 30 min CH_3I was added dropwise until the deep orange solution had decolorized. After a further 30 min at –78° the reaction mixture was poured into sat. aq. NH_4Cl-solution. Extraction (pentane), work-

up, and fractional distillation afforded **5b** as a colorless oil (290 mg, 85%), b.p. 90–100° (bath)/20 Torr, Rf (benzene) 0.73, GC. (108°): 2.7. – IR.: 2980, 1610, 1365, 1260, 1060. – ^{1}H-NMR.: 0.21 (9H); 0.98 (*t, J*=7, 3H); 2.13 (2 *qa, J*=7; irradation at 4.18→*qa, J*=7, 2H); 4.81 (*t, J*=7; irradiation at 2.13→*s*, 1H); 4.97 (*d*×*d, J*=10 and 2, 1H); 5.28 (*d*×*d, J*=17 and 2, 1H); 6.20 (*d*×*d, J*=17 and 10, 1H). – MS.: 170 (47, $C_9H_{18}OSi^{+\cdot}$), 169 (22), 156 (19), 155 (100), 127 (17); HR.: M^+: Found 170.1109; Calc. 170.1127.

cis-2-Ethyl-8-phenyl-3-triethylsilyloxy-8-azabicyclo[4.3.0]non-3-en-7,9-dione (**7**). A solution of 3-triethylsilyloxy-1,3-pentadiene (**6a**), prepared as described below (509 mg, 2.4 mol), and *N*-phenylmaleimide (346 mg, 2 mmol) in benzene (5 ml) was heated under reflux for 1 h. Chromatography of the evaporated solution (toluene/ethyl acetate 10:1) gave the cycloadduct **7** as a colorless oil (720 mg, 89%), Rf (toluene/ethyl acetate 3:1) 0.58. – IR.: 2950, 2860, 1715, 1500, 1377. – ^{1}H-NMR.: 0.5–1.2 (18H); 1.6–2.1. (2H); 2.4 (*m*, 2H); 2.65 (*d*×*d*×*d, J*=15, 6 and 3.5, irradiation at 4.84→*d*×*d, J*=15 and 3.5, 1H); 3.0–3.5 (*m*, irradiation at 2.4→*AB*-system, br., *J*=9.5, 2H); 4.84 (*m*, irradiation at 2.4→*d, J*=3, 1H); 7.2–7.5 (5H). – MS.: ($M^{+\cdot}$ not observed), 217 (20), 189 (17), 173 (26), 119 (90), 117 (100), 103 (43).

General procedure for the preparation and electrophilic substitution of 3-triethylsilyloxypentadienyllithium (**4a**). *(Table 1* and *2).* – A solution of *sec*-BuLi (1.0 mol-equiv.) in cyclohexane was added dropwise to a stirred 1.5M solution of **3a** in dry THF at –78° under Ar. After 30 min at –78° the electrophile (1.1 mol-equiv. unless otherwise specified) was added slowly to the deep orange solution. After a reaction time of 10 to 60 min at –78° the decolorized mixture was poured into sat. aq. NH_4Cl-solution. Extraction (pentane) and work-up gave the crude adduct(s) **8** and/or **6** which were purified by distillation or chromatography.

(*Z*)-*Triethylsilyloxy-1,3-pentadiene* (**6a**). To a solution of **4a**, prepared from **3a** (396 mg, 2 mmol) water was added at –78° until the solution had decolorized. The reaction mixture was immediately poured into sat. aq. NH_4Cl-solution to give after work-up and distillation at 90–100° (bath)/12 Torr the diene **6a** (oil, 346 mg, 87%), Rf (toluene) 0.76, GC. (112°): 8.53. – IR.: 2960, 2880, 1350, 1212, 1063. – ^{1}H-NMR.: 0.40–1.30 (15H); 1.68 (*d, J*=7, 3H); 4.82 (*t, J*=7, irradiation at 1.68→*s*, 1H); 4.95 (*d*×*d, J*=10 and 2, 1H); 5.30 (*d*×*d, J*=17 and 2, 1H); 6.20 (*d*×*d, J*=17 and 10, 1H). – MS.: 198 (47, $C_{11}H_{22}OSi^{+\cdot}$), 169 (100), 157 (30), 142 (35), 141 (94).

(*Z*)-*3-Triethylsilyloxy-5-trimethylsilyl-1,3-pentadiene* (**6b**). Starting from 2 mmol of **3a** and chlorotrimethylsilane the general procedure, followed by distillation at 150–160° (bath)/12 Torr, furnished **6b** (480 mg, 89%), Rf (hexane) 0.30, GC. (140°): 8.55. – IR. 2950, 2880, 1635, 1600, 1350, 1250, 1053, 940. – ^{1}H-NMR.: 0.02 (*s*, 9H); 0.58–1.13 (15H); 1.52 (*d, J*=8, 2H); 4.82 (*t, J*=8, irradiation at 1.52→*s*, 1H); 4.89 (*d*×*d, J*=10 and 2, 1H); 5.22 (*d*×*d, J*=17 and 2, 1H); 6.20 (*d*×*d, J*=17 and 10, 1H). – MS.: 270 (23, $C_{14}H_{30}OSi_2^{+\cdot}$), 189 (7), 175 (8), 140 (17), 115 (100), 87 (67).

(*Z*)-*5-Triethylsilyl-3-triethylsilyloxy-1,3-pentadiene* (**6c**). Starting from 2 mmol of **3a** and chlorotriethylsilane the general procedure, followed by distillation at 160–166° (bath)/12 Torr, furnished **6c** (oil, 540 mg, 87%), Rf (hexane) 0.38. GC. (180°): 8.56. – UV.: 249 (4.27). – IR.: 2960, 2880, 1640, 1602, 1415, 1350, 1050. – ^{1}H-NMR.: 0.4–1.3 (30H), 1.56 (*d, J*=8, 2H); 4.80 (*t, J*=8, 1H); 4.86 (*m*, 1H); 5.20 (*d*×*d, J*=17 and 2, 1H); 6.18 (*d*×*d, J*=17 and 10, 1H). – MS.: 312 (27, $C_{17}H_{36}OSi_2^{+\cdot}$), 217 (8), 168 (7), 140 (6), 115 (100), 87 (86).

(*Z*)-*3-Triethylsilyloxy-1,3-hexadiene* (**6d**). Starting from 10 mmol of **3a** and methyl iodide the general procedure, followed by distillation, gave **6d** (oil, 1.8 g, 85%), b.p. 96–98°/12 Torr, Rf (benzene) 0.69. GC (108°): 11.55. – UV.: 239.5 (3.99). – IR.: 2970, 2890, 1605, 1364, 1055. – ^{1}H-NMR.: 0.5–1.3 (18H); 2.16 (*m*, 2H); 4.76 (*t, J*=7, 1H), 4.97 (*d*×*d, J*=10 and 2, 1H); 5.30 (*d*×*d, J*=17 and 2, 1H); 6.19 (*d*×*d, J*=17 and 10, 1H). – MS.: 212 (28, $C_{12}H_{24}OSi^{+\cdot}$), 183 (52), 141 (19), 115 (25), 103 (100).

(*Z*)-*3-Triethylsilyloxy-1,3-heptadiene* (**6e**) *and 3-ethyl-3-triethylsilyloxy-1,4-pentadiene* (**8e**). Starting from 2 mmol of **3a** and ethyl iodide the general procedure, followed by distillation at 140° (bath)/12 Torr, gave a (2.76:1)-mixture of **6e** and **8e** (82%, analyzed by GC. and ^{1}H-NMR). Separation of this mixture by chromatography afforded the 1,4-diene **8e** (oil), Rf (hexane) 0.60, GC. (132°) 4.83. – IR.: 2960, 2880, 1470, 1420, 1045, 930. – ^{1}H-NMR.: 0.45–1.15 (18H); 1.64 (*qa, J*=7, 2H); 5.12 (*d*×*d, J*=10 and 2, 2H); 5.24 (*d*×*d, J*=17 and 2, 2H); 5.90 (*d*×*d, J*=17 and 10, 2H). – MS.: ($M^{+\cdot}$ not observed), 198 (19), 197 (100), 115 (30), 103 (73), 87 (36), 75 (54).

The more polar 1,3-diene **6e** (oil), Rf (hexane) 0.35, GC. (132°): 8.39. – IR.: 2960, 2885, 1647, 1606, 1370, 910. – ^{1}H-NMR.: 0.5–1.2 (18H); 1.41 (*m*, 2H); 2.13 (*qa, J*=7, 2H); 4,81 (*t, J*=7, 1H); 4.97 (*d*×*d, J*=10 and 2, 1H); 5.32 (*d*×*d, J*=17 and 2, 1H); 6.21 (*d*×*d, J*=17 and 10, 1H). – MS.: 226 (24, $C_{13}H_{26}OSi^{+\cdot}$), 197 (95), 155 (38), 115 (100), 103 (85), 87 (100); HR.: M^+: Found 226.1793; Calc. 226.1753.

(Z)-*Triethylsilyloxy-1,3-undecadiene* (**6f**) *and 3-hexyl-3-triethylsilyloxy-1,4-pentadiene* (**8f**). Following the general procedure, **4a**, prepared from **3a** (2 mmol), was treated with hexyl bromide. Distillation of the crude product mixture at 140–150° (bath)/12 Torr gave a (0.98:1.0)-mixture of **6f** and **8f** (82% total yield, analyzed by GC). Chromatography (hexane) gave the less polar α-product **8f** (164 mg, oil), Rf (hexane) 0.67, GC. (150°): 9.87. – IR. (film): 2960, 2880, 1470, 1100, 920, 750, 730. – ^{1}H-NMR.: 0.4–2.2 (28H); 5.08 (*d* × *d*, *J* = 10 and 2, 2H); 5.23 (*d* × *d*, *J* = 17 and 2, 2H); 5.87 (*d* × *d*, *J* = 17 and 10, 2H). – MS.: ($M^{+\cdot}$ not observed), 253 (70), 197 (100), 115 (30), 103 (49), 87 (33), 75 (26), 59 (15). Further elution furnished the more polar γ-product **6f** (202 mg, oil), Rf (hexane) 0.48, GC. (150°): 21.25. – IR.: 2930, 1604, 1370, 1055, 908. – UV.: 239 (4.21). – ^{1}H-NMR.: 0.5–1.8 (28H); 2.14 (*m*, 2H); 4.78 (*t*, *J* = 7, 1H); 4.95 (*d* × *d*, *J* = 10 and 2, 1H); 5.30 (*d* × *d*, *J* = 17 and 2, 1H); 6.18 (*d* × *d*, *J* = 17 and 10, 1H). – MS.: 282 (7, $C_{17}H_{34}OSi^{+\cdot}$), 253 (20), 197 (60), 115 (84), 103 (100), 87 (75).

(Z)-*6-Methyl-3-triethylsilyloxy-1,3-heptadiene* (**6g**) *and 3-triethylsilyloxy-3-isopropyl-1,4-pentadiene* (**8g**). Following the general procedure, **4a** prepared from **3a** (2 mmol), was treated with isopropyl iodide. Distillation of the crude product mixture at 150° (bath)/12 Torr gave a (0.29:1)-mixture of **6g** and **8g** (85% total yield, analyzed by GC.). Chromatography of this mixture (hexane) furnished the less polar α-product **8g** (oil), Rf (hexane) 0.78, GC. (132°): 6.32. – IR.: 2960, 2880, 1649, 1115, 1042, 933. – ^{1}H-NMR.: 0.4–1.2 (21H); 1.76 (*m*, 1H); 5.22 (*d* × *d*, *J* = 10 and 2, 2H); 5.26 (*d* × *d*, *J* = 17 and 2, 2H); 5.96 (*d* × *d*, *J* = 17 and 10, 2H). – MS.: ($M^{+\cdot}$ not observed), 211 (44), 197 (100), 157 (57), 115 (74), 103 (59), 87 (80). Further elution gave the more polar γ-product **6g** (oil), Rf (hexane) 0.40, GC. (132°): 9.48. – IR.: 2960, 2885, 1609, 1370, 1059. – UV.: 239.5 (4.21). – ^{1}H-NMR.: 0.5–1.2 (21H); 1.64 (*m*, 1H); 3.03 (*t*, *J* = 7, 2H); 4.83 (*t*, *J* = 7, 1H); 4.97 (*d* × *d*, *J* = 10 and 2, 1H); 5.31 (*d* × *d*, *J* = 17 and 2, 1H); 6.22 (*d* × *d*, *J* = 17 and 10, 1H). – MS.: 240 (13, $C_{14}H_{28}OSi^{+\cdot}$) 197 (32), 115 (100), 103 (24), 87 (83), 75 (27); HR. $M^{+\cdot}$: Found 240.1909; Calc. 240.1904.

(Z)-*Triethylsilyloxy-1,3,8-nonatriene* (**6h**) *and 3-triethylsilyloxy-3-vinyl-1,6-heptadiene* (**8h**). a) Following the general procedure, **4a**, prepared from **3a** (2 mmol), was treated with 4-bromo-1-butene. Distillation of the crude product mixture at 110–120° (bath)/12 Torr gave a (1.56:1)-mixture of **6h** and **8h** (80% total yield, analyzed by GC. and 60 MHz-^{1}H-NMR.). Chromatography of this mixture (hexane) furnished the less polar α-product **8h** (oil), Rf (hexane) 0.54, GC. (150°): 5.57. – IR.: 2960, 2880, 1644, 1415, 1040, 922. – ^{1}H-NMR.: 0.4–1.2 (15H); 1.68 (*m*, 2H); 2.08 (*m*, 2H); 4.8–5.25 (2H); 5.13 (*d* × *d*, *J* = 10 and 2, 2H); 5.26 (*d* × *d*, *J* = 17 and 2, 2H); 5.86 (*m*, 1H); 5.89 (*d* × *d*, *J* = 17 and 10, 2H). – MS.: ($M^{+\cdot}$ not observed), 223 (38), 197 (63), 115 (42), 103 (100), 87 (51), 75 (69). Further elution afforded the more polar γ-product **6h** (oil), Rf (hexane) 0.27, GC. (150°): 10.57. – IR.: 2960, 2880, 1642, 1605, 1363, 1052. – ^{1}H-NMR.: 0.5–1.2 (15H); 1.50 (*m*, 2H); 2.12 (*m*, 4H); 4.78 (*t*, *J* = 7; irradiation at 2.12 → *s*, 1H); 4.9–5.15 (2H); 5.07 (*m*, irradiation at 2.12 → *d* × *d*, *J* = 10 and 2, 1H); 5.30 (*d* × *d*, *J* = 17 and 2, 1H); 5.84 (*m*; irradiation at 2.12 → *d* × *d*, *J* = 17 and 10, 1H); 6.19 (*d* × *d*, *J* = 17 and 10, 1H). – MS.: 252 (6, $C_{15}H_{28}OSi^{+\cdot}$), 223 (20), 115 (52), 103 (100), 87 (77), 75 (53). b) A solution of 4-buten-1-ol (2.88 g, 0.04 mol) in dry pyridine (3 ml) was added dropwise to a stirred slurry of *p*-toluene sulfonylchloride (8.58 g, 0.045 mol) in pyridine (14 ml) at –5°. The reaction mixture was allowed to stand at 5° during 6.5 h, poured into cold water and extracted with ether. Work-up followed by distillation afforded 4-butenyl-*p*-toluenesulfonate (oil, 7.6 g, 84%), b.p. 115–117°/0.1 Torr, GC. (210°): 20.15. – IR.: 1600, 1365, 1180, 1100. – ^{1}H-NMR.: 2.41 (*m*, 2H); 2.45 (*s*, 3H); 4.08 (*t*, *J* = 7, 2 H); 5.07 (*d* × *d*, *J* = 10 and 2, 1H); 5.09 (*d* × *d*, *J* = 17 and 2, 1H); 5.72 (*m*, 1H); 7.3–7.9 (4H). – MS.: ($M^{+\cdot}$ not observed), 155 (55), 91 (85), 54 (97), 53 (52), 39 (100). Following the general procedure, **4a**, prepared from **3a** (1 mmol), was treated with 4-buten-1-yl-*p*-toluenesulfonate to give after distillation at 60–70° (bath)/0.01 Torr a 9.5:90.5-mixture of **6h** and **8h** (197 mg, 78% total yield, analyzed by GC.). The major product was identified as **8h** by ^{1}H-NMR. evidence. c) 4-Bromo-1-butene (675 mg, 5 mmol) was added dropwise to a stirred slurry of silver trifluoromethanesulfonate (1.03 g, 4 mmol) in dry ether (10 ml) at 25° under Ar in the dark. The reaction mixture was kept at 25° for 13 h and then was filtered through a small amount of silical gel. The evaporated filtrate gave after distillation at 50–60° (bath)/12 Torr the 4-butenyl-trifluoromethanesulfonate (350 mg, 34%). – IR.: 1425, 1355, 1220, 1150, 960. – ^{1}H-NMR.: 2.50 (*m*, 2H); 4.44 (*t*, *J* = 7, 2H); 4.9–5.3 (2H); 5,66 (*m*, 1H). Following the general procedure, **5**, prepared from **4a** (1 mmol), was treated with 4-butenyltrifluoromethanesulfonate to give after distillation at 60–70° (bath)/0.01 Torr a 2:98-mixture of **6h** and **8h** (179 mg, 71% total yield, analyzed by GC.).

(Z)-*Triethylsilyloxy-1,3,7-octatriene* (**6i**) *and 3-triethylsilyloxy-3-vinyl-1,5-hexadiene* (**8i**). Following the general procedure, **4a**, prepared from **3a** (2 mmol), was treated with allyl bromide to give after distillation at 60–90° (bath)/0.2 Torr a (2:1)-mixture of **6i** and **8i** (180 mg, 77% total yield, analyzed by GC.

and 60-MHz-^{1}H-NMR.). Chromatography (hexane) gave the less polar α-product **8i** (oil), Rf (hexane) 0.51, GC. (131°): 6.86. – IR.: 2960, 2880, 1642, 1410, 1040, 992. – ^{1}H-NMR.: 0.4–1.15 (15H); 2.41 (*d*×*t*, *J*=7 and 2, 2H); 5.06 (*m*, irradiation at 2.41 → *d*×*d*, *J*=7 and 2, 1H); 5.05–5.3 (3H); 5.25 (*d*×*d*, *J*=17 and 2, 2H); 5.81 (*m*, 1H); 5.92 (*d*×*d*, *J*=17 and 10, 2H). – MS.: ($M^{+\cdot}$ not observed), 209 (65), 197 (68), 115 (86), 103 (83), 87 (100), 75 (62). Further elution furnished the more polar γ-product **6i** (oil) Rf (hexane) 0.26, GC. (131°): 13.99. – IR.: 2960, 2880, 1655, 1605, 1365, 1052. – ^{1}H-NMR.: 0.5–1.2 (15H); 1.9–2.5 (4H); 4.80 (*t*, *J*=7; irradiation at 2.19 → *s*, 1H); 4.9–5.2 (2H); 5.11 (*m*; irradiation at 2.19 → *d*×*d*, *J*=10 and 2, 1H); 5.32 (*d*×*d*, *J*=17 and 2, 1H); 5.86 (*m*; irradiation at 2.19 → *d*×*d*, *J*=17 and 10, 1H); 6.20 (*d*×*d*, *J*=17 and 10, 1H). – MS.: 238 (4, $C_{14}H_{26}OSi^{+\cdot}$), 209 (13), 197 (57), 119 (78), 115 (100), 87 (87); HR.: M^+: Found 238.1762; Calc. 238.1753.

(*Z*)-*8-Methyl-3-triethylsilyloxy-1,3,7-nonatriene* (**6j**) *and 6-methyl-3-triethylsilyloxy-3-vinyl-1,5-heptadiene* (**8j**). Following the general procedure, **4a**, prepared from **3a** (2 mmol), was treated with 1-bromo-3-methyl-2-butene to give after distillation of the crude reaction mixture at 140–155° (bath)/12 Torr a (12:1)-mixture of **6j** and **8j** (76% total yield, analyzed by GC.). Chromatography of the crude product mixture gave the less polar α-product **8j** (oil, 20 mg), Rf (hexane) 0.47, GC. (150°): 7.30. – IR.: 2955, 2880, 1040, 920. – ^{1}H-NMR.: 0.4–1.2 (15H); 1.60 (*s*, 3H); 1.72 (*s*, 3H); 2.34 (br. *d*, *J*=7, 2H); 5.11 (*d*×*d*, *J*=10 and 2, 2H); 5.18 (*m*, 1H); 5.24 (*d*×*d*, *J*=17 and 2, 2H); 5.93 (*d*×*d*, *J*=17 and 10, 2H). – MS.: ($M^{+\cdot}$ not observed), 237 (10), 198 (17), 197 (100), 115 (78), 103 (22), 87 (73). Further elution afforded the more polar γ-product **6j** (oil, 235 mg), Rf (hexane) 0.29, GC. (150°): 16.06. – IR.: 2960, 2880, 1645, 1605, 1363, 1053. – ^{1}H-NMR.: 0.5–1.2 (15H); 1.61 (*s*, 3H); 1.70 (*s*, 3H); 2.11 (*m*, 4H); 4.79 (*t*, *J*=7; irradiation at 2.11 → *s*, 1H); 4.97 (*d*×*d*, *J*=10 and 2, 1H); 5.14 (*m*, 1H); 5.30 (*d*×*d*, *J*=17 and 2, 1H); 6.19 (*d*×*d*, *J*=17 and 10, 1H). – MS.: 266 (5, $C_{16}H_{30}OSi^{+\cdot}$), 197 (100), 169 (5), 116 (19), 115 (90), 87 (90); HR.: M^+: Found 266.2068; Calc. 266.2066.

(*Z*)-*3-Triethylsilyloxy-1,3,7,9-decatetraene* (**6k**) *and 6-triethylsilyloxy-6-vinyl-1,3,7-octatriene* (**8k**). Following the general procedure, **4a**, prepared from **3a** (2 mmol), was treated with 5-bromo-1,3-pentadiene [3] to give after distillation at 160–170° (bath)/12 Torr a (3:1)-mixture of **6k** and **8k** (76% total yield, analyzed by GC. and ^{1}H-NMR.). Chromatography of this mixture (hexane) gave the less polar α-product **8k** (oil), Rf (hexane) 0.46, GC. (150°): 10.15. – IR.: 2960, 2880, 1001, 925, 900. – ^{1}H-NMR.: 0.4–1.15 (15H); 2.44 (*d*×*d*, *J*=7, 2H); 4.9–5.5 (6H); 5.5–6.6 (5H). MS.: ($M^{+\cdot}$ not observed), 235 (7), 197 (86), 115 (86), 103 (22), 87 (100), 75 (24). Further elution afforded the more polar γ-product **6k** (oil) Rf (hexane) 0.25, GC. (150°): 22.38. – IR.: 2960, 2880, 1645, 1605, 1000, 900. – ^{1}H-NMR.: 0.5–1.2 (15H); 2.20 (*m*, 4H); 4.79 (*t*, *J*=7; irradiation at 2.20 → *s*, 1H); 4.9–5.5 (4H); 5.71 (*m*; irradiation at 2.20 → *d*×*d*, *J*=15, 1H); 5.9–6.6 (3H). – MS.: 264 (5, $C_{16}H_{28}OSi^{+\cdot}$), 235 (8), 197 (70), 169 (18), 115 (100), 87 (91); HR.: M^+: Found 264.1906; Calc. 264.1909.

(*Z*)-*6-Phenyl-3-triethylsilyloxy-1,3-hexadiene* (**6l**) *and 3-benzyl-3-triethylsilyloxy-1,4-pentadiene* (**8l**). Following the general procedure, **4a**, prepared from **3a** (2 mmol), was treated with benzyl chloride to give after distillation at 60–80° (bath)/0.5 Torr a (0.96:1)-mixture of **6l** and **8l** (84% total yield, analyzed by GC. and ^{1}H-NMR.). Chromatography of this mixture (hexane) gave the less polar α-product **8l** (oil), Rf (hexane) 0.29, GC. (180°): 13.23. – IR. (film): 3030, 2960, 2920, 2880, 1460, 1420, 1245, 1120, 1050, 1005, 925, 745, 730, 705. – ^{1}H-NMR.: 0.3–1.2 (15H); 2.92 (*m*, 2H); 5.14 (*d*×*d*, *J*=10 and 2, 2H); 5.22 (*d*×*d*, *J*=17 and 2, 2H); 5.99 (*d*×*d*, *J*=17 and 10, 2H); 7.50 (br. *s*, 5H). – MS.: ($M^{+\cdot}$ not observed), 259 (13), 197 (96), 126 (15), 119 (30), 115 (83), 105 (30), 103 (34), 91 (100), 87 (58). Further elution furnished the more polar γ-product **6l** (oil), Rf (hexane) 0.19, GC. (180°): 26.34. – IR.: 2960, 2880, 1645, 1605, 1052, 905, 696. – ^{1}H-NMR.: 0.5–1.2 (15H); 2.3–2.85 (4H); 4.82 (*t*, *J*=7, 1H); 4.98 (*d*×*d*, *J*=10 and 2, 1H); 5.32 (*d*×*d*, *J*=17 and 2, 1H); 6.19 (*d*×*d*, *J*=17 and 10, 1H); 7.1–7.5 (5H). – MS.: ($M^{+\cdot}$ not observed), 197 (91), 119 (98), 117 (100), 103 (85), 84 (75), 75 (79). Treatment of **5** with benzyl bromide under identical conditions furnished a mixture of **6l** and **8l**, containing slightly more of the α-product **8l** (^{1}H-NMR.-analysis).

(*Z*)-*5-Triethylsilyloxy-4,6-heptadien-1-ol* (**6m**) *and 3-triethylsilyloxy-3-vinyl-4-penten-1-ol* (**8m**). Ethyleneoxide was introduced into a solution of **4a** (prepared from 2 mmol of **3a**) in THF at –78° under Ar until the mixture has decolorized. The usual quenching and work-up furnished a colorless oil which contained **6m** and **8m** in a ratio of 0.7:1 (87% total yield, analyzed by GC. and 60 MHz-^{1}H-NMR.). Chromatography of the crude mixture (CH_2Cl_2) gave the less polar α-product **8m** (oil, 210 mg), Rf (CH_2Cl_2) 0.30, GC. (187°): 6.46. – IR.: 3530 br., 2960, 2890, 1015, 938. – ^{1}H-NMR.: 0.4–1.2 (15H); 1,90 (*t*, *J*=6, 2H); 2.78 (br. *s*, disappears on exchange with D_2O, 1H); 3.80 (br. *t*, *J*=6, 2H); 5.22 (*d*×*d*, *J*=10 and 2, 2H); 5.30 (*d*×*d*, *J*=17 and 2, 2H); 5.95 (*d*×*d*, *J*=17 and 10, 2H). MS.: ($M^{+\cdot}$ not observed), 213 (35), 197

(27), 103 (100), 87 (25), 75 (85). Further elution furnished the more polar γ-product **6m** (oil, 170 mg), Rf (CH_2Cl_2) 0.20, GC. (187°): 11.13. – UV.: 238.5 (4.14). – IR.: 3635, 3470 br., 1646, 1603, 1364, 1054, 908. – ^{1}H-NMR.: 0.4–1.1 (15H); 1.4–2.3 (4H); 2.14 (br. *s*, disappears after exchange with D_2O, 1H); 4.08 (*t*, *J*=7, 2H); 4.82 (*t*, *J*=6, 1H); 4.97 (br. *d*, *J*=10, 1H); 5.42 (br. *d*, *J*=17, 1H); 6.07 (*d*×*d*, *J*=17 and 10, 1H). – MS.: (M^+· not observed), 242 (7), 213 (33), 197 (9), 185 (11), 157 (16), 115 (20), 110 (13), 103 (100), 91 (9), 87 (27), 59 (21), 55 (44), 45 (25).

(Z)-4-Triethylsilyloxy-3,5-hexadien-1-ol (**6n**) *and 2-triethylsilyloxy-2-vinyl-3-buten-1-ol* (**8n**). Gaseous formaldehyde was condensed into a stirred solution of **4a** (prepared from 2 mmol of **3a**) at –78° under Ar. The reaction mixture was allowed to attain 0° during 3 h. The usual quenching and work-up of the decolorized reaction mixture furnished a (83:17)-mixture of **6n** and **8n** (analyzed by 60-MHz-^{1}H-NMR.) which was chromatographed (CH_2Cl_2) to give the less polar α-product **8n** (oil, 96 mg), Rf (toluene/ethyl acetate 9:1) 0.27. – IR. 3560, 2950, 2880, 1420, 1220, 932. – ^{1}H-NMR.: 0.4–1.2 (15H); 1.98 (br. *s*, disappears after exchange with D_2O, 1H); 3.54 (*m*, exchange with D_2O or irradiation at 1.98 → *s*, 2H); 5.28 (*d*×*d*, *J*=10 and 2, 2H); 5.33 (*d*×*d*, *J*=17 and 2, 2H); 5.97 (*d*×*d*, *J*=17 and 10, 2H). – MS.: (M^+· not observed), 198 (32), 196 (33), 115 (32), 103 (100), 87 (44), 75 (75). Further elution afforded the more polar γ-product **6n** (oil, 288 mg), Rf (toluene/ethyl acetate 9:1) 0.52. – IR.: 3620, 2960, 2880, 1645, 1604, 1370, 1060. – UV.: 238 (4.16). – ^{1}H-NMR.: 0.4–1.2 (15H); 1.76 (*s*, disappears after exchange with D_2D, 1H); 2.44 (*qa*, *J*=7, 2H); 3.68 (*t*, *J*=7; irradiation at 2.42 → *s*, 2H); 4.85 (*t*, *J*=7, irradiation at 2.42 → *s*, 1H); 5.03 (*d*×*d*, *J*=10 and 2, 1H); 5.35 (*d*×*d*, *J*=17 and 2, 1H); 6.22 (*d*×*d*, *J*=17 and 10, 1H). – MS.: 228 (7, $C_{12}H_{24}O_2Si^+$·), 197 (33), 184 (10), 103 (100), 87 (37), 75 (100).

(Z)-5-Triethylsilyloxy-4,6-heptadien-2-ol (**6o**) *and 3-triethylsilyloxy-3-vinyl-4-penten-2-ol* (**8o**). Following the general procedure, **4a**, prepared from **3a** (2 mmol), was treated with acetaldehyde. Chromatography of the crude product mixture (CH_2Cl_2) gave the less polar α-product **8o** (oil, 12 mg), Rf (toluene/ethyl acetate 3:1) 0.49. – IR.: 3550, 2960, 2880, 1420, 1010. – ^{1}H-NMR.: 0.4–1.1 (15H); 1.13 (*d*, *J*=7, 3H); 2.52 (br. *s*, disappears after exchange with D_2O, 1H); 3.78 (*qa*, *J*=7, 1H); 5.19 (*d*×*d*, *J*=10 and 2, 2H); 5.35 (*d*×*d*, *J*=17 and 2, 2H); 5.99 (*d*×*d*, *J*=17 and 10, 2H). – MS.: (M^+· not observed), 213 (24), 159 (76), 115 (87), 103 (100), 87 (70), 75 (63). Further elution afforded the more polar γ-product **6o** (oil, 426 mg), Rf (toluene/ethyl acetate 3:1) 0.27. – IR.: 3450 br., 2960, 2880, 1650, 1610, 1060, 1012. – ^{1}H-NMR.: 0.4–1.15 (15H); 1.21 (*d*, *J*=7, 3H); 1.94 (*s*, disappears after exchange with D_2O, 1H); 2.30 (*t*, *J*=7, 2H); 3.86 (*m*, irradiation at 1.21 → *t*, *J*=6.5, 1H); 4.87 (*t*, *J*=7, irradiation at 2.30 → *s*, 1H); 5.03 (*d*×*d*, *J*=10 and 2, 1H); 5.34 (*d*×*d*, *J*=17 and 2, 1H); 6.23 (*d*×*d*, *J*=17 and 10, 1H). – MS.: 242 (12, $C_{13}H_{26}O_2Si^+$·), 213 (9), 198 (37), 197 (100), 169 (13).

(Z)-6-Triethylsilyloxy-5,7-octadien-3-ol (**6p**) *and 4-triethylsilyloxy-4-vinyl-5-hexen-3-ol* (**8p**). Following the general procedure, **4a**, prepared from **3a** (4 mmol), was treated with propanal. Chromatography of the crude product mixture gave the less polar α-product **8p** (oil, 144 mg), Rf (toluene/ethyl acetate 9:1) 0.62. – IR.: 3560, 2960, 2880, 1240, 930. – ^{1}H-NMR.: 0.5–1.1 (18H); 1.1–1.8, 2H); 2.46 (*m*, disappears after exchange with D_2O, 1H); 3.46 (*m*, 1H); 5.1–5.5 (4H); 6.00 (*d*×*d*, *J*=17 and 10, 2H). – MS.: (M^+· not observed), 227 (30), 197 (36), 115 (65), 103 (100), 87 (58), 75 (68). Further elution afforded the more polar γ-product **6p** (oil, 786 mg), Rf (toluene/ethyl acetate 9:1) 0.38. – IR.: 3600 br., 2960, 2880, 1640, 1602, 1360, 1052. – ^{1}H-NMR.: 0.4–1.2 (18H); 1.52 (*m*, 2H); 2.15 (br. *s*, disappears after exchange with D_2O, 1H); 2.31 (*m*, 2H); 3.60 (*m*, 1H); 4.91 (*t*, *J*=7, 1H); 5.03 (*m*, 1H); 5.34 (*m*, 1H); 6.24 (*m*, 1H). – MS.: 256(6, $C_{14}H_{28}O_2Si^+$·), 227 (13), 197 (61), 115 (100), 103 (54), 87 (77).

(Z)-7-Triethylsilyloxy-6,8-nonadien-4-ol (**6q**) *and 3-triethylsilyloxy-3-vinyl-1-hepten-4-ol* (**8q**). Following the general procedure, **4a**, prepared from **3a** (4 mmol), was treated with butanal. Chromatography of the crude product mixture (CH_2Cl_2) gave the less polar α-product **8q** (oil, 164 mg), Rf (toluene/ethyl acetate 9:1) 0.68. – IR. 3560, 2960, 2880, 1238, 938. – ^{1}H-NMR.: 0.4–1.1 (18H); 1.1–1.9 (4H); 2.49 (*d*, *J*=3, disappears after exchange with D_2O, 1H); 3.46 (*m*, 1H); 5.2–5.55 (4H); 6.06 (*m*, 2H). – MS.: (M^+· not observed), 241 (27), 197 (38), 115 (63), 103 (100), 87 (56), 75 (65). Further elution afforded the more polar γ-product **6q** (oil, 754 mg), Rf (toluene/ethyl acetate 9:1) 0.46. – UV.: 238 (4.24). – IR.: 3600, 2960, 2880, 1603, 1065, 920. – ^{1}H-NMR.: 0.5–1.2 (18H); 1.2–1.8 (4H); 1.99 (br. *s*, disappears after exchange with D_2O, 1H); 2.30 (*m*, 2H); 3.68 (*m*, 1H); 4.91 (*t*, *J*=7, 1H); 5.03 (*d*×*d*, *J*=10 and 2, 1H); 5.35 (*d*×*d*, *J*=17 and 2, 1H); 6.23 (*d*×*d*, *J*=17 and 10, 1H). – MS.: 270(3, $C_{15}M_{30}O_2Si^+$·), 241 (7), 197 (61), 169 (22), 115 (100), 103 (62).

(Z)-1-Phenyl-4-triethylsilyloxy-3,5-hexadien-1-ol (**6r**) *and 1-phenyl-2-triethylsilyloxy-2-vinyl-3-buten-1-ol* (**8r**). Following the general procedure, **4a**, prepared from **3a** (4 mmol), was treated with freshly distilled benzaldehyde. Chromatography of the crude product mixture (CH_2Cl_2) furnished the less polar α-

product **8r** (oil, 82 mg), Rf (toluene/ethyl acetate 9:1) 0.63. – IR. (film): 2955, 2910, 2875, 1420, 1125, 1005, 730, 700. – ^{1}H-NMR.: 0.4–1.2 (15H); 3.10 (*2s*, disappear after exchange with D_2O, 1H); 4.57 (*m*, 1H); 5.1–5.5 (4H); 5.7–6.25 (2H); 7.2–8.0 (5H). – MS.: (M^+· not observed), 275 (6), 217 (34), 169 (23), 115 (17), 106 (73), 105 (80), 103 (57), 91 (36), 77 (100), 75 (67). Further elution furnished the more polar γ-product **6r** (oil, 890 mg), Rf (toluene/ethyl acetate 9:1) 0.41. – UV.: 239 (4.09). – IR.: 3610 br., 2960, 2880, 1060, 710. – ^{1}H-NMR.: 0.4–1.2 (15H); 2.37 (br. *s*, disappears after exchange with D_2O, 1H); 2.59 (*m*, 2H); 4.69 (*t*, J=7, irradiation at 2.59 → *s*, 1H); 4.84 (*t*, J=7, irradiation at 2.59 → *s*, 1H); 5.01 (*d*× *d*, J=10 and 2, 1H); 5.34 (*d*× *d*, J=17 and 2, 1H); 6.19 (*d*× *d*, J=17 and 10, 1H); 5.1–5.5 (5H). – MS.: (M^+ not observed), 198 (33), 197 (30), 172 (100), 171 (29), 169 (41).

(Z)-2-Methyl-5-triethylsilyloxy-4,6-heptadien-2-ol (**6s**) *and 2-methyl-3-triethylsilyloxy-3-vinyl-4-penten-2-ol* (**8s**). Following the general procedure, **4a**, prepared from **3a** (4 mmol), was treated with acetone. Chromatography of the product mixture (CH_2Cl_2) gave the less polar α-product **8s** (oil, 27 mg), Rf (toluene/ethyl acetate 9:1) 0.61. – IR.: 3570, 2950, 2880, 1370, 1102, 930. – ^{1}H-NMR.: 0.5–1.1 (15H); 1.14 (*s*, 6H); 2.32 (*s*, disappears after exchange with D_2O, 1H); 5.33 (*d*× *d*, J=10 and 2, 2H); 5.36 (*d*× *d*, J=17 and 2, 2H; 6.20 (*d*× *d*, J=17 and 10, 2H). – MS.: (M^+· not observed), 227 (32), 169 (34), 115 (37), 103 (100), 87 (40), 75 (60). Further elution furnished the more polar γ-product **6s** (oil, 842 mg), Rf (toluene/ethyl acetate 9:1) 0.24. – IR.: 3460 br., 2960, 2880, 1650, 1612, 1370, 1012. – ^{1}H-NMR.: 0.4–1.2 (15H); 1.22 (*s*, 6H); 2.02 (br., *s*, disappears after exchange with D_2O, 1H); 2.32 (*d*, J=7, 2H); 4.92 (*t*, J=7; irradiation at 2.32 → *s*, 1H); 5.02 (*d*× *d*, J=10 and 2, 1H); 5.34 (*d*× *d*, J=17 and 2, 1H); 6.24 (*d*× *d*, J=17 and 10, 1H). – MS.: 256 (3, $C_{14}H_{28}O_2Si^+$), 241 (7), 227 (24), 198 (77), 169 (100).

(Z)-1-(3-triethylsilyloxy-2,4-pentadienyl)-1-cyclohexanol (**6t**) *and 1-(1-triethylsilyloxy-1-vinyl-2-propenyl)-1-cyclohexanol* (**8t**). Following the general procedure, **4a**, prepared from **3a** (4 mmol), was treated with cyclohexanone. Chromatography of the product mixture (CH_2Cl_2) gave the less polar α-product **8t** (oil, 38 mg), Rf (toluene/ethyl acetate 9:1) 0.68. – IR.: 3560, 2940, 2885, 1157, 1126, 930. – ^{1}H-NMR.: 0.5–1.1 (15H); 1.1–1.8 (10H); 1.98 (*s*, disappears after exchange with D_2O, 1H); 5.2–5.5 (4H); 6.19 (*d*× *d*, J=17 and 10, 2H). – MS.: (M^+ not observed), 267 (17), 198 (32), 169 (66), 115 (25), 103 (100), 75 (66). Further elution furnished the more polar γ-product **6t** (oil, 879 mg), Rf (toluene/ethyl acetate 9:1) 0.41. – UV.: 239 (4.09). – IR.: 3480 br., 2950, 2890, 1647, 1610, 1060. – ^{1}H-NMR.: 0.5–1.2 (15H); 1.52 br. (*s*, 11 H); 2.32 (*d*, J=8, 2H); 4..96 (*t*, J=8, irradiation at 2.32 → *s*, 1H); 5.04 (*d*× *d*, J=10 and 2, 1H); 5.35 (*d*× *d*, J=17 and 2, 1H); 6.26 (*d*× *d*, J=17 and 10, 1H). – MS.: (M^+· not observed), 198 (28), 169 (32), 164 (22), 119 (100), 117 (100).

(Z)-1,1-Diphenyl-4-triethylsilyloxy-3,5-hexadien-1-ol (**6u**). According to the general procedure, **4a**, prepared from **3a** (4 mmol), was treated with benzophenone. Chromatography of the reaction mixture (CH_2Cl_2) gave the γ-product **6u** as the only isolable product (oil, 1.31 g, 89%), Rf (toluene) 0.26. – IR.: 3550 br., 2960, 2880, 1648, 1605, 1060. – ^{1}H-NMR.: 0.4–1.2 (15H); 2.68 (*s*, disappears after exchange with D_2O, 1H); 3.16 (*d*, J=7, 2 H); 4.76 (*t*, J=7, 1H); 5.00 (*d*× *d*, J=10 and 2, 1H); 5.34 (*d*× *d*, J=17 and 2, 1H); 6.13 (*d*× *d*, J=17 and 10, 1H); 7.1–7.6 (10H). – MS.: (M^+· not observed), 217 (12), 207 (58), 183 (17), 182 (17), 105 (100).

Attempted interconversion of (*Z*)-7-triethylsilyloxy-6,8-nonadien-4-ol (6q) and 3-triethylsilyloxy-3-vinyl-1-hepten-4-ol (8q). – a) A solution of the α-product **8q** (108 mg, 4 mmol) in THF (1 ml) was added to a freshly prepared solution of lithium hexamethyldisilazane (4 mmol) in THF (2 ml). The mixture was stirred at –78° for 1 h. Quenching with sat. aq. NH_4Cl-solution and work-up gave unchanged **8q**. None of the isomer **6q** could be detected by TLC. b) The γ-product **6q** was subjected to identical reaction condition as described above. Work-up gave unchanged **6q** and no **8q** according to TLC. and ^{1}H-NMR.-evidence. c) *sec*-BuLi (1 mol-equiv.) was added to a solution of **8q** in THF at –100°. The solution was kept at –78° for 1 h. A sample showed no formation of the isomer **6q** by TLC. After warming the reaction mixture slowly to 0° and work-up, no isomer **6q** was detected by TLC.evidence.

Attempted conversion of 2-triethylsilyloxy-2-vinyl-3-buten-1-ol (8n) into 4-triethylsilyloxy-3,5-hexadien-1-ol (6n). – A solution of **8n** (15 mg, 0.66 mmol) in THF (0.25 ml) was added to a freshly prepared solution of lithium hexamethyldisilazane (0.66 mmol) in THF (0.25 ml) at –78°. Then gaseous formaldehyde was condensed into the mixture which subsequently was allowed to warm to 0° over 1 h with vigorous stirring. Quenching with aq. NH_4Cl-solution and work-up gave unchanged **8n** and no **6n** according to TLC. and ^{1}H-NMR.

Reaction of 3-triethylsilyloxypentadienyllithium (4a) with acyl chlorides *(Schemes 6* and *7).* – *(3Z,8Z)-6-Ethyl-3,9-bis(triethylsilyloxy)-1,3,8,10-undecatetraen-6-ol* (**9a**). A solution of **4a**, prepared from

3a (2 mmol) in THF (7 ml) was added dropwise to stirred propionyl chloride (1.85 g, 20 mmol) at –78° under Ar. After 30 min at –78° the reaction mixture was poured into cold sat. aq. $NaHCO_3$-solution. Extraction with ether, work-up and chromatography (CH_2Cl_2) gave, as the major product **9a** (oil, 196 mg, 43% yield), Rf (CH_2Cl_2) 0.38. – IR.: 3560, 2960, 2880, 1640, 1602, 1052, 1006. – ^{1}H-NMR.: 0.5–1.2 (33H); 1.52 (*qa, J*=7, 2H); 1.80 (br., *s,* disappears after exchange with D_2O, 1H); 2.32 (*d, J*=7, 4H); 4.92 (*t, J*=7; irradiation at 2.32 → *s,* 2H); 5.01 (*d*× *d, J*=10 and 2, 2H); 5.34 (*d*× *d, J*=17 and 2, 2H); 6.23 (*d*× *d, J*=17 and 10, 2H).

(3Z),8Z)-6-Propyl-3,9-bis(triethylsilyloxy)-1,3,8,10-undecatetraen-6-ol (**9b**). A solution of **4a**, prepared from **3a** (2 mmol), in THF (7 ml) was added dropwise to stirred butyryl chloride (2.45 g, 20 mmol) at –78° under Ar. After 30 min at –78° the reaction mixture was poured into cold sat. aq. $NaHCO_3$-solution. Extraction with ether, work-up and chromatography (CH_2Cl_2) gave, as the major product **9b** (oil, 292 mg, 62%), Rf (CH_2Cl_2) 0.44. – IR.: 3560, 2960, 2880, 1640, 1602, 1056, 910. – ^{1}H-NMR.: 0.4–1.2 (33H); 1.43 (*m,* 4H); 2.00 br. (*s,* disappears after exchange with D_2O, 1H); 2.20 (*d, J*=7, H); 4.90 (*t, J*=7, 2H); 5.00 (*d*× *d, J*=10 and 2, 2H); 5.32 (*d*× *d, J*=17 and 2, 2H); 6.23 (*d*× *d, J*=17 and 10, 2H). – MS.: (M^+· not observed), 269 (16), 217 (18), 198 (16), 103 (100), 87 (45), 75 (73).

(Z)-3-Triethylsilyl-1-vinyl-1-propenyl acetate (**10**). A solution of **4a**, prepared from **3a** (2 mmol), in THF (6 ml) was added dropwise during 15 min to stirred acetyl chloride (2.2 g, 28 mmol) at –78° under Ar. The reaction mixture was then added carefully to cold, excess sat. aq. $NaHCO_3$-solution. Extraction with ether, work-up and chromatography (toluene) gave **10** (pale yellow oil, 360 mg, 75%), Rf (toluene) 0.32, GC. (171°): 9.49. – IR.: 2960, 2880, 1765, 1205, 1035. – ^{1}H-NMR.: 0.4–1.05 (15H); 1.48 (*d, J*=8, 2H); 2.25 (*s,* 3H); 4.95 (*d, J*=10, 1H); 4.99 (*d, J*=17, 1H); 5.42 (*t, J*=8; irradiation at 1.48 → *s,* 1H); 6.25 (*d*× *d, J*=17 and 10, 1H). – MS.: 240 (35, $C_{13}H_{24}O_2Si^+$·), 197 (35), 119 (69), 117 (74), 115 (100); HR.: M^+: Found 240.1546; Calc. 240.1545.

Preparation of 5-substituted-1-penten-3-ones 11 *(Schemes 7* and *8, Table 3). – 5-Triethylsilyl-1-penten-3-one* (**11c**). *Cleavage of the acetate* **10**. A solution of **10** (240 mg, 1 mmol) in dimethoxyethane was added dropwise, during 10 min, to a solution of methyllithium (2.5 mmol) in dimethoxyethane (8 ml) at +10° under Ar. The reaction mixture was allowed to stand for a further 15 min at +10° and then was poured into cold sat. aq. NH_4Cl-solution. Successive extraction with ether, work-up and chromatography (CH_2Cl_2) and distillation at 80–100° (bath)/2 Torr gave the enone **11c** (oil, 168 mg, 85%), Rf (toluene) 0.27, GC. (5% *Carbowax,* 140°): 11.55. – IR.: 2960, 2880, 1710, 1692, 1620, 1418, 1403, 1087, 1020, 990, 970, 960, 718. – ^{1}H-NMR.: 0.4–1.1 (17H); 2.57 (*m,* 2H); 5.82 (*d*× *d, J*=9 and 3, 1H); 6.0–6.6 (2H). – MS.: (M^+· not observed), 169 (100), 141 (9), 115 (9), 113 (17), 103 (12), 99 (11), 87 (17), 75 (23), 67 (12), 59 (17), 55 (14).

Cleavage of the silyl ether **6c**. KF (69.6 mg, 1.2 mmol) was added portionwise to a stirred solution of **6c** (312 mg, 1 mmol) in methanol (15 ml) at –10° under Ar. The reaction mixture was allowed to attain 0° during 2 h and then was poured into cold water. Extraction (ether), work-up, chromatography (CH_2Cl_2), and distillation at 80–100° (bath)/2 Torr gave the enone **11c** (168 mg, 85%) identical to a sample prepared by the procedure A.

5-Trimethylsilyl-1-penten-3-one (**11b**). KF (174 mg, 3 mmol) was added portionwise to a stirred solution of **6b** (540 mg, 2 mmol) in methanol (20 ml) at –5°, under Ar. After 1 h at –5° to 0° the reaction mixture was poured into cold water. Extraction with CH_2Cl_2 work-up, rapid chromatography (CH_2Cl_2) and distillation at 80–90° (bath)/12 Torr gave the enone **11b** (oil, 281 mg, 90% yield), Rf (CH_2Cl_2) 0.46. – IR.: 1705, 1680, 1620, 1400, 1250, 1085. – ^{1}H-NMR.: 0.0 (*s,* 9H); 0.5–1.1 (2H); 2.56 (*m,* 2H); 5.81 (*d*× *d, J*=9 and 3, 1H); 5.1–5.6 (2H). – MS.: 156 (12, $C_8H_{16}OSi^+$·), 155 (55), 141 (100), 127 (16), 117 (57), 99 (31).

1-Undecen-3-one (**11f**). KF (58 mg, 1 mmol) was added to a stirred solution of the diene **6f** (190 mg, 0.67 mmol) in methanol (10 ml) at –10°. The reaction mixture was stirred at –10° to –5° during 3 h and then was poured into cold sat. aq. NaCl-solution. Extraction with ether, work-up and distillation at 120–140° (bath)/15 Torr furnished the enone **11f** (88 mg, 78%), Rf (toluene) 0.37, GC. (150°): 7.08. – IR.: 2930, 2860, 1690, 1618, 990, 960. – ^{1}H-NMR.: 0.89 *t, J*=7, 3H); 1.29 (br. *s,* 10H); 1.62 (*m,* 2H); 2.59 (*t, J*=7, 2H); 5.80 (*d*× *d, J*=9 and 3, 1H); 6.0–6.6 (2H). – MS.: 168 (1, $C_{11}H_{20}O^+$·), 139 (9), 97 (7), 83 (14), 70 (100), 55 (59). Comparison of the ^{1}H-NMR. and MS. data of **11f** with those published [20] for undecenone, isolated from *Dictyopteris,* confirmed the identity of **11f** with the natural product.

8-Methyl-1,7-nonadien-3-one **11j**. *Method (A):* KF (87 mg, 1.5 mmol) was added to a stirred solution of the silyl ether **6j** (266 mg, 1 mmol) in methanol (10 ml) at –10° under Ar. After 1 h at –10° to 0° the reaction mixture was poured into cold sat. aq. NaCl-solution. Extraction with ether, work-up, chromato-

graphy (CH_2Cl_2) and distillation at 80–100° (bath)/12 Torr gave the enone **11j** (112 mg, 74%), Rf (toluene) 0.24, GC. (120°): 12.32. – IR.: 2930, 1702, 1686, 1400, 951. – ^{1}H-NMR.: 0.8–1.35 (2H); 1.61 (br. *s*, 3H); 1.71 (br. *s*, 3H); 2.00 (*m*, 2H); 2.58 (*t*, *J*=7, 2H); 5.12 (br. *t*, *J*=7, 1H); 5.81 (*d*×*d*, *J*=9 and 3, 1H); 6.0–6.6 (2H). – MS.: 152 (2, $C_{10}H_{16}O)^{+\cdot}$, 121 (3), 119 (9), 117 (9), 82 (100), 67 (50).

Method B: KF (44 mg, 0.75 mmol) was added to a stirred solution of the **6j** (106 mg, 0.4 mmol) in 2-propanol (1.5 ml) at 0° under Ar. The reaction mixture was allowed to attain +25° during 1 h. After stirring the mixture at +25° for 16 h it was poured into cold water. Extraction with ether, work-up and chromatography (CH_2Cl_2) gave the enone **11j** (42 mg, 70%), identical (GC., TLC. ^{1}H-NMR., IR.) to a sample prepared by *Method A*.

6-Hydroxy-1-hepten-3-one (**11o**). KF (290 mg, 5 mmol) was added portionwise to a stirred solution of the silyl ether **6o** (968 mg, 4 mmol) in methanol (20 ml) at –10° under Ar. The reaction was stirred at –10° to –5° during 1 h and then was poured into cold sat. aq. NaCl-solution. Extraction with ether, work-up and chromatography (ethyl acetate) gave the hydroxyenone **11o** (oil, 390 mg, 80%), Rf (EtOAc) 0.50. – IR.: 3450 br., 2970, 1683, 1405, 958. – ^{1}H-NMR.: 1.22 (*d*, *J*=7, 3H); 2.80 (*m*, 2H); 3.60 br. (*s*, disappears after exchange with D_2O, 1H); 3.76 (*t*, *J*=7; irradiation at 2.80 → *s*, 2H); 3.84 (*m*; irradiation at 2.80 → *q*, *J*=7, 1H); 5.85 (*d*×*d*, *J*=9 and 3, 1H); 6.0–6.6 (2H). – MS.: ($M^{+\cdot}$ not observed), 110 (31), 109 (7), 95 (12), 83 (15), 66 (19), 55 (100).

1-Methoxy-6-phenyl-3-hexanone. A (1:1)-mixture of **6l** and **8l** was prepared from **4a** (obtained from 2 mmol of **3a** as described above. KF (128 mg, 2.2 mmol) was added to a stirred solution of this mixture of **6l** and **8l** in methanol (10 ml) at 0°. The reaction mixture was allowed to attain 15° during 15 h and then was poured into water. Successive extraction with ether, work-up and chromatography (toluene, toluene-EtOAc 9:1) gave *1-methoxy-6-phenyl-3-hexanone* (oil, 125 mg, 30% yield from **3a**, Rf (toluene/EtOAc 9:1) gave *1-methoxy-6-phenyl-3-hexanone* (oil, 125 mg, 30% yield from **3a**, Rf 0.38 (toluene/EtOAc 9:1). – IR. 2930, 1720, 1460, 1130, 710. – ^{1}H-NMR.: 1.92 (*m*, 2H); 2.46 (*t*, *J*=7.5, 2H); 2.62 (*t*, *J*=6, 2H); 2.64 (*t*, *J*=6, 2H); 3.32 (*s*, 3H); 3.62 (*t*, *J*=6; irradiation at 2.62 → *s*, 2H); 7.05–7.5 (5H). – MS.: ($M^{+\cdot}$ not observed), 188 (10), 147 (9), 119 (22), 104 (100), 102 (80).

Preparation of the substituted silyloxydienes 14 *(Scheme 9).* – *(4E)-1,4-Hexadien-3-ol* (**13a**). A solution of crotonaldehyde (700 mg, 10 mmol) in THF (10 ml) was added dropwise to a mechanically stirred slurry of vinylmagnesium bromide (freshly prepared at 0°, 12 mmol) in THF (25 ml) at 0° under Ar. After 30 min at 0° the reaction mixture was poured into cold sat. aq. NH_4Cl-solution. Extraction with ether, work-up and distillation at 110–130° (bath)/15 Torr gave **13a** (oil, 568 mg, 62%). – IR.: 3600 br., 2910, 2850, 960, 918. – ^{1}H-NMR.: 1.73 (*d*, *J*=7, 3H); 1.76 (br. *s*, disappears after exchange with D_2O, 1H); 4.59 (br. *t*, *J*=6, 1H); 5.14 (*d*×*t*, *J*=10 and 2, 1H); 5.27 (*d*×*t*, *J*=17 and 2, 1H); 5.3–6.2 (3H). – MS.: 98 (11, $C_6H_{10}O^{+\cdot}$), 97 (22), 83 (88), 71 (40), 69 (50) 55 (100).

(4E)-3-Triethylsilyloxy-1,4-hexadiene (**14a**). The alcohol **13a** (230 mg, 2.35 mmol) was silylated as described for the preparation of **3a** to give, after distillation at 120° (bath)/12 Torr, 480 mg of **14a** (oil, 97%), Rf (toluene) 0.74. – IR.: 2960, 2880, 1122, 970, 925. – ^{1}H-NMR.: 0.4–1.15 (15H); 1.70 (*d*, *J*=6, 3H); 4.56 (br., *t*, *J*=6, 1H); 5.05 (*d*×*t*, *J*=10 and 2; irradiation at 4.56 → *d*×*d*, *J*=10 and 2, 1H); 5.20 (*d*×*t*, *J*=17 and 2; irradiation at 4.56 → *d*×*d*, *J*=17 and 2, 1H); 5.3–5.9 (2H); 5.86 (*m*, irradiation at 4.56 → *d*×*d*, *J*=17 and 10, 1H). – MS.: ($M^{+\cdot}$ not observed), 197 (9), 183 (70), 103 (100), 87 (1), 75 (4).

2-Methyl-3-triethylsilyloxy-1,4-pentadiene (**14b**). 2-Methylacrylaldehyde (prepared by oxidation of 2-methyl-2-propenyl alcohol with MnO_2 [32], 3.8 g, 54.3 mmol) was treated with vinylmagnesium bromide, as described for the preparation of **13a** to give after distillation at 150° (bath)/16 Torr **13b** (oil, 4.2 g, 79%. – IR.: 3600, 3430 br., 1112, 1050, 985) which after silylation (as described for the preparation of **4a**) and distillation furnished **14b** (3.42 g, 81%), b.p. 90–92°/16 Torr, Rf (hexane) 0.31, GC. (117°): 4.33. – IR.: 2935, 1450, 1407, 916, 890. – ^{1}H-NMR.: 0.4–1.2 (15H); 1.68 (*d*, *J*=1.5, 3H); 4.54 (*d*, *J*=6, 1H); 4.82 (*t*, *J*=1.5, 1H); 5.01 (*m*, 1H); 5.0–5.4 (2H); 5.83 (*d*×*d*×*d*, *J*=17, 10 and 6, 1H). – MS. 189 (5. $C_{12}H_{24}OSi^{+\cdot}$), 184 (16), 183 (100), 103 (47), 75 (32).

5-Methyl-1,4-hexadien-3-ol (**13c**). 3,3-Dimethylacrylaldehyde (588 mg, 7 mmol) was treated with vinylmagnesium bromide, as described for the preparation of **13a** to give after distillation the alcohol **13c** (oil, 545 mg, 70%), b.p. 55–56°/11 Torr, Rf (EtOAc) 0.63. – IR.: 3590, 3400 br., 2970, 1380, 990, 927. – H-NMR.: 1.70 br., *s*, disappears after exchange with D_2O, 1H); 1.72 (*d*, *J*=1, 3H); 1.76 (*d*, *J*=1, 3H); 4.86 (*d*×*d*, *J*=7 and 6; irradiation at 5.92 → *d*, J=7, 1H); 5.09 (*d*×*t*, *J*=10 and 2, 1H); 5.23 (*m*, irradiation at 1.72 → *d* *J*=9, 1H); 5.24 (*m*, 1H); 5.92 (*d*×*d*×*d*, *J*=17, 10 and 6, 1H). – MS.: 112 (20, $C_7H_{12}O^{+\cdot}$), 97 (100), 85 (36), 83 (46), 79 (40), 69 (38).

5-Methyl-3-triethylsilyloxy-1,4-hexadiene (**14c**). The alcohol **13c** (515 mg, 4.6 mmol) was silylated as described for the preparation of **4a** to give **14c** after distillation (760 mg, 73%), b.p. 93–95°/Torr, Rf (toluene) 0.64, GC. (118°): 7.32. – IR. 2955, 2880, 1380, 1240, 922. – ^{1}H-NMR.: 0.4–1.2 (15H); 1.68 (*d*, *J*= 1, 3H); 1.72 (*d*, *J*= 1, 3H); 4.7–5.4 (4H); 5.85 (*d*× *d*× *d*, *J*= 17, 10 and 6, 1H). – MS.: 226 (16, $C_{13}H_{26}OS^{+\cdot}$), 197 (18), 189 (10), 115 (10), 103 (100), 75 (39).

3-(1-Cyclohexenyl-3-triethylsilyloxy)-1-propene (**14d**). Subsequent treatment of 1-cyclohexene-1-carbaldehyde with vinylmagnesium bromide and chlorotriethylsilane as described for the preparation of **14a** furnished, after distillation at 140–150° (bath)/0.1 Torr, **14d** (oil), Rf (hexane) 0.28. – ^{1}H-NMR.: 0.4–1.2 (15H); 1.63 (*m*, 4H); 2.05 (*m*, 4H); 4.49 (br. *d*, *J*=6, 1H); 5.09 (*d*× *t*, *J*= 10 and 2; irradiation at 4.49 → *d*× *d*, *J*= 10 and 2, 1H); 5.25 (*d*× *t*, *J*= 17 and 2; irradiation at 4.49→ *d*× *d*, *J*= 17 and 2, 1H); 5.73 (*m*, 1H); 5.86 (*d*× *d*× *d*, *J*= 17, 10 and 6; irradiation at 4.49 → *d*× *d*, *J*= 17 and 10, 1H). – MS.: 252 (4, $C_{15}H_{28}OSi^{+\cdot}$), 223 (36), 217 (9), 189 (7), 103 (100), 87 (11).

Preparation and electrophilic substitution of the triethylsilyloxyhexadienyllithium 15 *(Scheme 10).* – (*2Z,4E*)-*3-Triethylsilyloxy-2,4-hexadiene* **16a** and (*3Z*)-*3-Triethylsilyloxy-1,3-hexadiene* (**17a** = **6d**). A solution of *sec*-BuLi (0.5 mmol) in cyclohexane was added dropwise to a stirred solution of the diene **14a** (105 mg, 0.5 mmol) in THF (1.5 ml) at –78° under Ar. After 10 min water was added to the orange reaction mixture at –78°. Then the decolorized mixture was poured into sat. aq. NH_4Cl-solution. Extraction with pentane and work-up gave a (4:1)-mixture of **16a** and **17a** (= **6d**) (102 mg, 96% total yield, analyzed by GC. and ^{1}H-NMR.). Chromatography (hexane) gave the less polar product **17a** (= **6d**, 4 mg) identical (TLC., GC., IR., ^{1}H-NMR.) to a sample of **6d**, prepared by methylation of **4a**. Further elution gave the more polar product **16d** (oil, 82 mg), Rf (hexane) 0.16, GC. (118°): 9.8. – IR. (film): 2955, 2915, 2880, 1045, 1005, 745. – ^{1}H-NMR.: 0.5–1.4 (15H); 1.65 (*d*, *J*=7, 3H); 1.75 (*d*, *J*=6, 3H); 4.72 (br. *qa*, *J*=7; irradiation at 1.65 → *s*, 1H); 5.85 (*m*, 2H). – MS.: 212 (12, $C_2H_{24}OSi^{+\cdot}$), 197 (17), 189 (10), 183 (43), 103 (100), 75 (60).

(*2E,4Z*)-*4-Triethylsilyloxy-2,4-heptadiene* (**16b**). A solution of *sec*-BuLi (0.5 mmol) in cyclohexane was added dropwise to a stirred solution of the diene **14a** (105 mg, 0.5 mmol) in THF (1.5 ml) at –78° under Ar. After 15 min at –78°, methyliodide was added until the orange reaction mixture had decolorized. Then the mixture was poured into sat. aq. NH_4Cl-solution. Extraction with pentane, work-up and distillation at 130–140° (bath)/15 Torr, gave the product **16b** (oil, 106 mg, 95%, analyzed by GC. to be 97% pure), Rf (hexane) 0.19, GC. (127°): 8.99. – UV.: 237 (3.83). – IR. (film): 2965, 2910, 2875, 1005, 745. – ^{1}H-NMR.: 0.4–1.3 (18H); 1.75 (*d*, *J*=6, 3H); 2.12 (*qi*, *J*=7, 2H); 4.62 (*t*, *J*=7; irradiation at 2.12 → *s*, 1H); 5.5–6.2 (2H). – MS.: 226 (4, $C_{13}H_{26}OSi^{+\cdot}$), 207 (18), 189 (16), 183 (31), 161 (9), 115 (7), 103 (100), 75 (69).

Reaction of the anion 15 with benzaldehyde. – A solution of *sec*-BuLi (0.5 mmol) in cyclohexane was added dropwise to a stirred solution of the diene **14a** (105 mg, 0.5 mmol) in THF (1.5 ml) at –78° under Ar. After 10 min at –78° a solution of benzaldehyde (64 mg, 0.6 mmol) in THF (1 ml) was added to the orange solution. The decolorized reaction mixture was then poured into sat. aq. NH_4Cl-solution. Extraction with ether and work-up gave an unseparable oil (154 mg, 97% yield) which on ^{1}H-NMR. analysis (250 MHz) appears to be a (1:1)-mixture of *1-phenyl-4-triethylsilyloxy-3,5-heptadien-1-ol* (**16c**) and *2-methyl-1-phenyl-4-triethylsilyloxy-3,5-hexadien-1-ol* (**17c**) (3:2)-stereoisomer mixture). This analysis is based on integration of the signals at 5.00 (*d*× *d*, *J*= 10 and 2, minor isomer **17c**); 5.06 (*d*× *d*, *J*= 10 and 2, major isomer **17c**); 5.31 (*d*× *d*, *J*= 17 and 2, minor isomer **17c**); 5.39 (*d*× *d*, *J*= 17 and 2); 6.15 (*d*× *d*, *J*= 17 and 10, major isomer **17c**); 6.23 (*d*× *d*, *J*= 17 and 10, minor isomer **17c**) as compared with the signals between 5.72–5.95 (attributed to **16c**).

Attempted lithiation/substitution of the silyloxydienes 14b to 14d. – The dienes **14b** and **14d** were treated with *sec*-BuLi followed by water or methyl iodide as described for the preparation of **16a** and **16b**. This sequence was also carried out in THF/HMPA or in THF/TMEDA. After work-up only unchanged **14b** to **14d** could be isolated.

Intramolecular[4 + 2]-cycloaddition reactions *(Schemes 12* and *13).* – *2-Triethylsilyloxybicyclo[4.3.0]non-1-ene* (**19**). A) *Preparation from* **6h**. A solution of the triene **6h** (252 mg, 1 mmol) in toluene was heated in a silylated, sealed pyrex tube at 160° during 17 h. Evaporation of the solution and distillation of the residue at 100–120° (bath)/0.03 Torr furnished **19** (oil, 212 mg, 84%), Rf (toluene) 0.73, GC. (148°): 18.47. – IR.: 2960, 2880, 1250, 1185. – ^{1}H-NMR.: 0.4–1.2 (15H); 1.3–2.8 (13H). – ^{13}C-NMR. (25.2 MHz): 141.2 *(s)*, 112 *(s)*, 41.6 *(d)*, 34.5 *(t)*, 29.8 *(t)*, 29.2 *(t)*, 26.6 *(t)*, 23.9 *(t)*, 6.8 *(m)*, 5.8 *(m)*. – MS.: 252 (76, $C_{15}H_{28}OSi^{+}$), 223 (33), 197 (26), 119 (38), 103 (100); HR.: M^+: Found 252.1909; Calc. 252.1948.

B) *Preparation by isomerisation of* **18**. A solution of **18** (63 mg, 0.25 mmol) in toluene (10 ml) was heated at 170° during 17 h in a silylated, sealed pyrex tube. Evaporation of the solution and distillation of the residue furnished **19** (52 mg, 82%) identical (TLC., GC.–coinjection, IR.: ^{1}H-NMR., ^{13}C-NMR.) to **19,** prepared from **6h** (method A).

cis-*Bicyclo[4.3.0]nonan-2-one* (**20**). A) *Preparation by silylether cleavage of* **19**. A solution of **19** (252 mg, 1 mmol) in methanol (4 ml) was added dropwise to a stirred solution of KF (75 mg, 1.3 mmol) in methanol (4 ml) at –5°. The reaction mixture was allowed to attain +5° during 2 h and then was poured into cold water. Extraction with ether, work-up, chromatography (CH_2Cl_2 p.p.) and distillation at 60–70° (bath)/0.1 Torr gave **20** (oil, 112 mg, 81%), Rf (toluene) 0.16, GC. (148°): 9.04. – IR.: 2940, 2870, 1710, 1450. – ^{1}H-NMR.: 1.2–2.1 (10H); 2.2–2.75 (4H). – MS.: 138 (38, $C_9H_{14}O^{+\cdot}$), 110 (29), 97 (100), 95 (44), 67 (63).

B) *Preparation by hydrogenation of* **22**. A solution of **22** (100 mg, 0.74 mmol) in ethanol (filtered through neutral Al_2O_3) was stirred with Pd/C (10%) (20 mg) at 1 atm. and 25° for 18 h. Filtration of the solution through *Celite,* evaporation, chromatography (benzene) of the residue and distillation gave **20** identical (TLC., GC., IR., ^{1}H-NMR.) to a sample of **20** prepared from **19** (method A).

Bicyclo[4.3.0]non-1(6)-en-2-one (**22**). 4-(1-Cyclopentenyl)butanoic acid [21] (680 mg, 4.4 mmol) was heated in polyphosphoric acid [33] (prepared by addition of P_2O_5 (7.5 g) to 85% H_3PO_4 (3 ml)) at 65° for 3 h. The reaction mixture was poured into cold water and extracted with ether. Work-up, chromatography (benzene/EtOAc 9:1) and distillation at 60° (bath)/0.03 Torr gave **22** (oil, 266 mg, 36%), Rf (toluene/EtOAc 9:1) 0.23, GC. (148°): 16.2. – IR.: 2940, 1680, 1640, 1400. – ^{1}H-NMR.: 1.2–2.2 (6H); 2.2–2.6 (6H). – MS.: 136 (49, $C_9H_{12}O^{+\cdot}$), 111 (15), 108 (100), 80 (11), 79 (27).

2-Triethylsilyloxybicyclo[4.3.0]non-2-ene (**18**). A solution of **20** (138 mg, 1 mmol) in THF (0.4 ml) was added dropwise to a stirred solution of lithium diisopropylamide (freshly prepared from diisopropylamine and BuLi, 1 mmol) in THF (2 ml) at –78° under Ar. After 40 min at –78° HMPA (0.3 ml) was added to the yellow solution followed by the addition of triethylsilyl chloride (225 mg, 1.3 mmol). The reaction mixture was allowed to attain +25° during 1 h and then poured into cold sat. aq. NH_4Cl-solution. Extraction with pentane, work-up and distillation at 60–70° (bath)/0.03 Torr gave the **18** (oil, 164 mg, 65%), Rf (toluene) 0.73. – IR.: 2960, 2880, 1672, 1250, 1193, 1022. – ^{1}H-NMR.: 0.5–1.15 (15H); 1.2–2.4 (12H); 4.81 (*t, J*=7, 1H). – MS.: 252 (36, $C_{15}H_{28}OSi^{+\cdot}$), 223 (20), 156 (8), 119 (44), 103 (100), 87 (18); HR. M^+: Found 252.1899; Calc. 252.1909.

cis-*Bicyclo[4.40]dec-7-en-2-one* (**23**). KF (128 mg, 2.2 mmol) was added portionwise during 5 min to a stirred solution of the tetraene **6k** (518 mg, 2 mmol) in methanol (25 ml) at –10°. After 1 h between –10° and 0° the mixture was poured into icewater. Extraction with ether, work-up, chromatography (CH_2Cl_2) and distillation at 70–80° (bath)/0.1 Torr gave the bicyclic ketone **23** (oil 235 mg, 78%), Rf (CH_2Cl_2) 0.27, GC. (150°): 19.03. – IR.: 2940, 2880, 1710, 1130. – ^{1}H-NMR.: 1.1–2.9 (12H); 5.50 (*d*×*m, J*=11, 1H); 5.72 (*d*×*m, J*=11, 1H); 5.72 (*d*×*m, J*=11, 1H). – ^{13}C-NMR. (25.2 MHz): 212.1 *(s),* 129.7 *(d),* 128.3 *(d),* 48.1 *(d),* 40.6 *(t),* 37.4 *(d),* 29.7 *(t),* 23.4 *(t),* 23.1 *(t),* 22.3 *(t).* – MS.: 150 (100, $C_{10}H_{14}O^{+\cdot}$), 135 (28), 122 (28), 91 (43), 79 (50); HR.: M^+: Found 150.1014; Calc. 150.1044. Cleavage of **6k** with KF in CD_3OD using the reaction conditions as described above furnished **23** showing no incorporated deuterium (IR., ^{1}H-NMR., MS.).

cis-*Bicyclo[4.4.0]decan-2-one* (**24**). *Method A.* Tris(triphenylphosphine) rhodium I chloride [23] (9.2 mg, 0.01 mmol) was added to a degassed solution of **23** (75 mg, 0.5 mmol) in dry benzene (4 ml) at 25° under Ar. This mixture was stirred under H_2 (1 atm.) during 36 h and then filtered through *Celite.* Work-up, chromatography (CH_2Cl_2) and distillation at 70° (bath)/0.1 Torr afforded **24** (oil, 65 mg, 86%) Rf (CH_2Cl_2) 0.28, GC. (150°): 17.91. – IR.: 2940, 2860, 1715, 1455. – ^{1}H-NMR.: 1.0–2.45 (15H); 2.55 (*qa, J*=7, 1H). – ^{13}C-NMR. (25.2 MHz): 212.7, 50.8, 40.6, 39.2, 29.3, 25.3, 24.7, 23.5, 23.2. – MS.: 152 (41, $C_{10}H_{16}O^{+\cdot}$), 123 (12), 110 (55), 109 (22), 97 (100). *cis*-Bicyclo[4.4.0]decan-2-one (**24**) did not epimerize to its *trans*-isomer **25** under the conditions (Pd/C, H_2, EtOH) which transform **23** to **25**.

Method B. A solution of all-*cis*-bicyclo[4.4.0]decanol (31 mg, 0.2 mmol), prepared by successive treatment of **23** with $NaBH_4$/EtOH and H_2/Pd/EtOH (as described below), in dry CH_2Cl_2 (1 ml) was added in one portion to a rapidly stirred slurry of pyridinium chlorochromate [34] (63 mg, 0.3 mmol) and NaOAc (anh., 328 mg, 4 mmol) in dry CH_2Cl_2 (6 ml) at 25° under Ar. After 30 min the reaction mixture was poured into ether. Filtration through *Celite,* work-up and chromatography (CH_2Cl_2) afforded the *cis*-**24** (28 mg, 91%), identical to a sample of **24** prepared from **23** *(Method A).*

Method C. – A solution of CrO_3 (0.6 g) in water (0.5 ml) was added dropwise to stirred pyridine (6 ml) at 0°. To this solution, at 0° was added a solution of all-*cis*-bicyclo[4.4.0]decan-2-ol (308 mg, 2 mmol,

prepared as described in [35]) in pyridine (1 ml). The reaction mixture was allowed to attain 25° during 30 min, left at 25° for a further 2 h and then was poured into cold water. Extraction with ether, work-up, chromatography (benzene) and distillation gave the ketone **24** (270 mg, 90% yield) identical to a sample of **24** prepared from **23** (method A).

*All-*cis*-bicyclo[4.4.0]dec-7-en-2-ol.* A solution of $NaBH_4$ (19 mg) in ethanol (2 ml) was added dropwise to a stirred solution of **23** (75 mg, 0.5 mmol) in ethanol (3 ml) at 0° under Ar. After 1 h at 0° the reaction mixture was poured into cold water. Extraction with ether and work-up gave all-*cis*-bicyclo[4.4.0]dec-7-en-2-ol (colorless solid, 68 mg, 90%), m.p. 55–65°, Rf (EtOAc) 0.52. – IR.: 3620, 3360 br., 3015, 2927, 2850, 1070, 1048, 860. – ^{1}H-NMR.: 0.9–1.9 (9H); 1.50 (br. *s*, disappears after exchange with D_2O, 1H); 1.9–2.25 (3H); 3.80 (*m*, 1H); 5.67 (*m*, 2H). – MS.: 152 (7, $C_{10}H_{16}O^+$), 134 (97), 119 (31), 92 (100), 91 (79), 79 (45).

*All-*cis*-bicyclo[4.4.0]decan-2-ol.* A solution of all-*cis*-bicyclo[4.4.0]dec-7-en-2-ol (50 mg, 0.3 mmol) in abs. ethanol (4 ml) was stirred with Pd/C (10%, 10 mg) under H_2 (1 atm.) for 12 h at 25°. Filtration through *Celite* and work-up gave all-*cis*-bicyclo[4.4.0]decan-2-ol (45 mg, 88%, colorless crystalline solid), m.p. 80–84°, Rf (EtOAc) 0.51. – IR.: 3620, 3400 br., 1451, 1057, 1030, 940. – ^{1}H-NMR.: 0.9–2.0 (16H); 1.44 (br. *s*, disappears after exchange with D_2O, 1H); 3.68 (*m*, 1H). – MS.: 154 (14, $C_{10}H_{18}O^{+\cdot}$), 136 (100), 121 (26), 95 (36), 94 (58), 81 (34).

trans-*bicyclo[4.4.0]decan-2-one* (**25**). *Method A.* A solution of **23** (75 mg, 0.5 mmol) in abs. ethanol was stirred with Pd/C (10%, 10 mg) under H_2 (1 atm.) for 12 h at 25°. Filtration through *Celite*, work-up, chromatography and distillation at 50–60°/0.1 Torr gave **25** (oil, 63 mg, 843%), Rf (CH_2Cl_2) 0.29, GC. (150°): 16.97. – IR.: 2920, 2850, 1715, 1450, 1315, 1201, 905. – ^{1}H-NMR.: 0.9–2.6 (16H). – ^{13}C-NMR. (25.2 MHz): 211.7, 55.1, 45.0, 41.8, 34.5, 33.1, 26.5, 25.9, 25.5, 25.2. – MS.: 152 (70, $C_{10}H_{16}O^{+\cdot}$), 134 (19), 123 (22), 109 (100), 97 (44), 81 (63).

Method B. Jones' reagent [36] (7.4 mmol) was added dropwise, during 5 min to a stirred solution of all-*cis*-bicyclo[4.4.0]decan-2-ol, prepared as described in [35], (1 g, 6.5 mmol) in acetone (12 ml) at 0°. After 30 min the reaction mixture was poured into cold water. Extraction with ether, work-up and distillation *i. v.* afforded **25** (oil, 860 mg, 85%) which crystallized on standing, m.p. 31–33°. The spectral and chromatographic properties are identical to those of a sample prepared from **23** *(Method A).*

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