83. Synthesis of 2-Norzizaene and 9,10-Dehydro-2-norzizaene (7,7-Dimethyl-6-methylidenetricyclo[6.2.1.$0^{1,5}$]undec-9-ene) *via* Intramolecular Allyl Cation Induced Cycloaddition[1])

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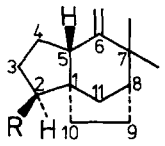
(18.I.83)

Summary

7,7-Dimethyl-6-methylidenetricyclo[6.2.1.$0^{1,5}$]undec-9-ene (**10**) has been prepared from allylic alcohol **8** in one step in 16% yield. Selective hydrogenation of **10** with diazene gives the 2-norzizaenes **1a** and **11**.

Zizaene (**1b**) and its oxygenated derivatives **1c–d** including the norsesquiterpenoid khusimone (**1e**) are important olfactory constituents of vetiver oil, and they are also excellent insect repellents [2]. Notable structural features of the compact tricyclic skeleton of **1** include *(i)* the *trans*-perhydroindan moiety, which also occurs in gibberellins, steroids, vitamin D and its derivatives, *(ii)* an accumulation of tertiary and quaternary C-atoms, C(1) also being a spiro centre and, very important, *(iii)* the crowded methylidene bond which tends to shift into the 5,6-position under thermodynamic conditions [3]. Despite a number of syntheses [4a–h], practical



1a R = H
1b R = CH_3
1c R = CH_2OH
1d R = CO_2H
1e R, H = O

approaches to **1** remain a special challenge and call for new synthetic methods. We describe a short route to **1a** in which the key reaction is an intramolecular cycloaddition of an allyl cation to a functionalized cyclopentadiene. In this approach the desired skeleton of **1** is 'over-synthesized' initially, because its precursor, 9,10-didehydro-2-norzizaene (**10**) contains a C(9),C(10)-double bond which is useful in its own right and can also be hydrogenated.

1. Model studies. – Having shown previously that alkylated bicyclo[3.2.1]octa-2,6-dienes can be prepared readily from allylic alcohols and cyclopentadiene in

[1]) Preliminary account: [1].
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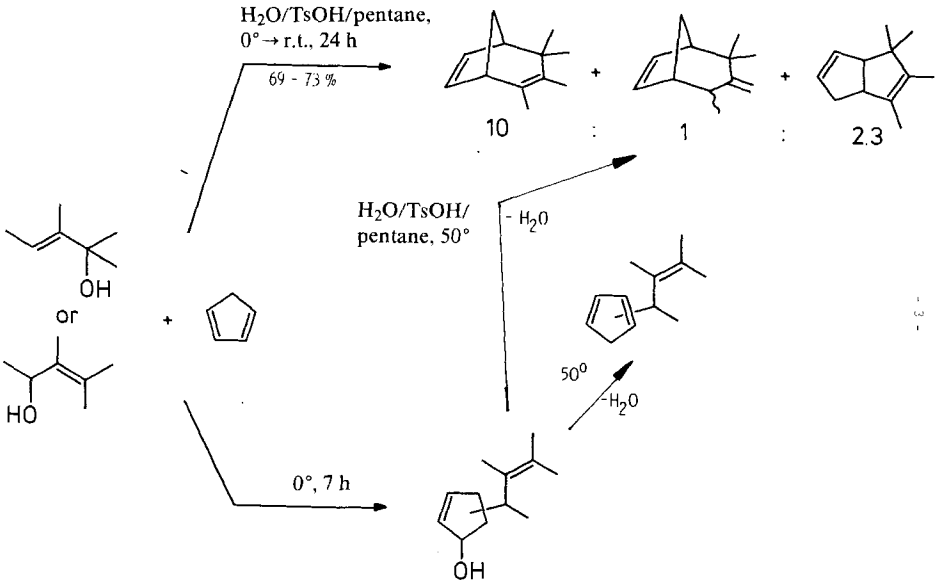
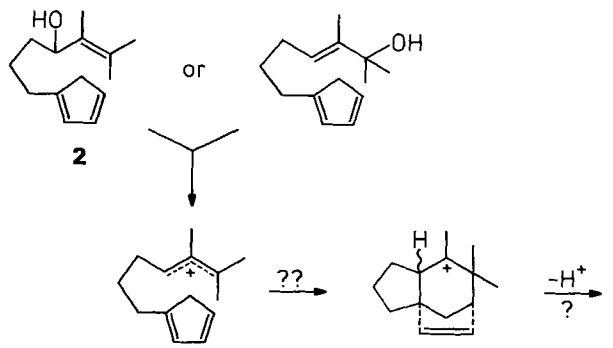
aqueous acid/pentane, *i.e.* under two-phase conditions [5] *(Scheme 1)* our synthetic plan was to intramolecularize this reaction as shown in *Scheme 2.* An experimental test of this concept required access to 7-(1,3-cyclopentadienyl)-2,3-dimethyl-2-hepten-4-ol (**2**), which was obtained as outlined *(Scheme 3).* Using methods developed during the initial phase of the model work *(Scheme 1)* and also the more selective method of ionization *via* trifluoroacetylation of **2** followed by treatment with zinc halide [8] we found six isomeric hydrocarbons of the desired formula $C_{14}H_{20}$ by GC./MS., but all six compounds were formed in traces only. We had surmised initially that the tricyclization in *Scheme 2* should benefit from intramolecularity compared with the model reaction in *Scheme 1.* However, the desired reaction did not occur to any significant extent. Apparently, strain in the tricycle **10** is too high, owing to the 9,10-double bond.

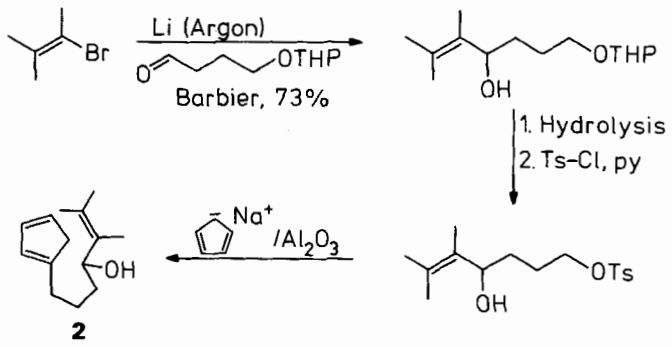
Scheme 1



Scheme 2



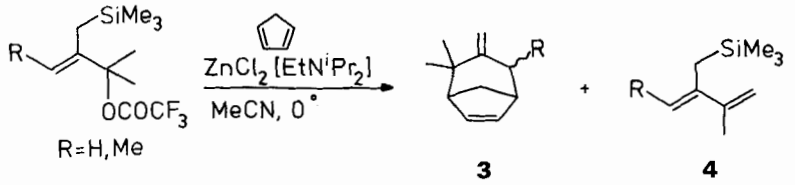
Scheme 3



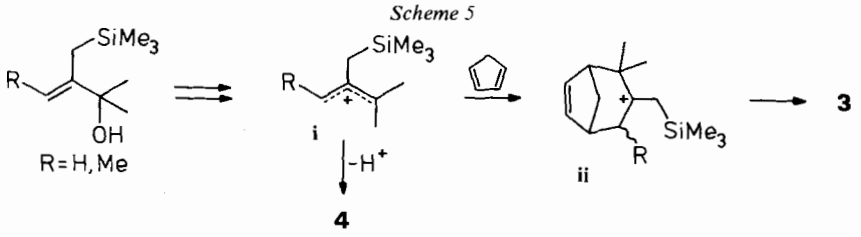
Lithiation of 2-bromo-3-methyl-2-butene under Ar [6a] is preferable to lithiation under N_2 [6b]. Yields of allylic alcohol are highest when the functionalized aldehyde is trapped *in situ*, *i.e.* under *Barbier* conditions. The primary alcoholic terminus of the aldehyde was also protected as benzyl ether which was cleaved under basic conditions (Na, liquid NH_3/THF) [7].

More driving force and better control in the generation of the methylidene double bond could be expected for reactions with 2-silylmethylallyl alcohols: appropriate intermolecular model reactions are summarized in *Scheme 4* [9]. The formation of adduct **3** is assumed to involve at least two cations, namely allyl cation **i**, which reacts with cyclopentadiene to give the stabilized tertiary cation **ii** and thence **3** *(Scheme 5)*. Formation of acyclic diene **4** could be kept at a minimum by allowing the reaction to proceed at low temperature in the absence of ethyldiisopropylamine.

Scheme 4



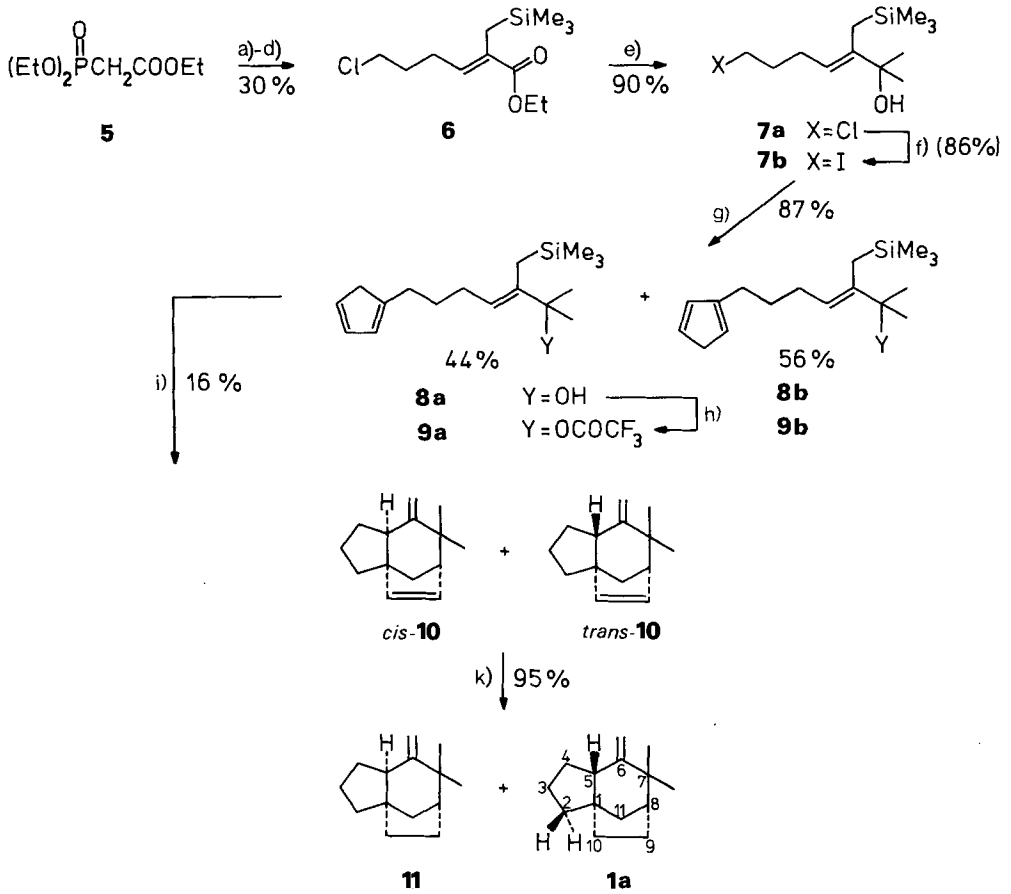
Scheme 5



2. Preparation of precursor *8* and intramolecular cycloaddition. – The functionalized acrylic ester **6** was obtained in a single flask reaction in 30% yield by *(i)* deprotonation of (diethylphosphono)acetate with sodium hydride in 1,2-di-

methoxyethane (DME), *(ii)* alkylation with iodomethyl(trimethyl)silane, *(iii)* renewed deprotonation and *(iv) Horner-Wittig* reaction with 4-chlorobutanal. Although the overall yield is only moderate (30%) – the crude product contained unreacted 4-chlorobutanal, which probably enolizes partially during the reaction – the route is highly convergent, because the potential leaving group (Cl), the α,β-unsaturated ester precursor of the tertiary allylic alcohol and the required silyl group are all joined in a single step. Treatment of **6** with an excess of methyllithium at $-30°$ gave allylic alcohol **7a** (90% yield), which was converted into **7b** (Cl/I exchange, 86%) by refluxing with sodium iodide in acetone. Treatment of **7b** with cyclopentadienylsodium in THF (3 h, 0°) afforded a valence tautomeric mixture of the 1- and 2-alkylated 1,3-cyclopentadienes **8a** and **8b** (87% after chro-

Scheme 6



a) NaH, DME, 0°; b) Me_3SiCH_2I, 70°, 3 h; c) NaH, 0° to r.t.; d) $ClCH_2CH_2CH_2CHO$, 0° to r.t.; e) >2 eq. MeLi, Et_2O, $-30°$; f) NaI, acetone, reflux, 48 h; g) cyclopentadienylsodium, THF, 3 h, 0°; h) $(CF_3CO)_2O$, $EtNPr^i_2$, CH_2Cl_2, $-70°$ to $-40°$; i) $ZnCl_2$/neutr. alumina, CH_2Cl_2/pentane, $-30°$; k) N_2H_2, MeOH, r.t.

matography). ^{1}H-NMR. and especially ^{13}C-NMR. showed the presence of **8a** and **8b** in a ratio of 44:56 [10]. When stored as a dilute solution in pentane at −20°, **8** did not decompose or polymerize significantly.

The key intramolecular double annulation **8** → **10** was first tried by treating the highly sensitive trifluoroacetate **9** (IR. band at 1775 cm^{-1}) prepared at −70 to −50°, with anhydrous $ZnCl_2$ at 0° in acetonitrile, as in the model work [9]. In order to suppress undesired intermolecular reactions we used **9** in high dilution (*ca.* 1 mmol of **9** in 60 ml of acetonitrile). GC. examination of crude product showed a complex mixture. We then found that trifluoroacetate **9** did not survive when its dilute solution (obtained from **8**, trifluoroacetic anhydride and ethyldiisopropylamine at −50 to −70°) was chromatographed on a dry column of basic alumina (activity I), cooled to −70°. A pale yellow oil, stable at r.t. was isolated (9.6% yield after distillation), which proved to be a *ca.* 1:1 mixture of *trans*- and *cis*-**10**. Apparently, the active surface and the heat of adsorption evolved on passing the dilute solution of **9** through the column, sufficed to promote the desired S_N1-like ionization of trifluoroacetate **9a**. However, the bulk of **9** decomposed and polymerized on the dry column.

Finally, neutral alumina (activity I) was coated with anhydrous $ZnCl_2$, suspended in pentane and the reaction solution of **9** was passed down the column at −30° and eluted slowly with pentane. An isomeric mixture of *trans*- and *cis*-**10** (ratio 1.15:1) was thus obtained in a reproducible yield of 15.7% with respect to total **8a**+**8b** (35.7% with respect to **8a** only). Another experiment with ZnI_2 on alumina instead of $ZnCl_2$ at −55°, gave a somewhat lower yield, but the more favourable ratio of *trans*-**10**/*cis*-**10** = 1.3:1.

Instead of **9** we also used the alcohol **8** directly by treating it with $TiCl_4$ and *N*-methylaniline in dichloromethane at −60 to −10° [11]. Apart from a major amount of polymer and allylic chloride the desired tricycle **10** was formed in 6% isolated yield (*trans*-**10**/*cis*-**10** = 1:1.2).

Pure tricyclic *trans*-**10**/*cis*-**10** is a colourless liquid with a fresh, characteristic odour reminiscent of camphor. When exposed to air the compounds assumed a yellow coloration within a few days, also at −20°. For storage it was converted into the silver nitrate complex which is stable at −20° (see below).

3. ^{1}H-NMR. spectroscopic identification of *10*. – In the 90-MHz ^{1}H-NMR. spectrum of **10** *(Fig. 1)* the geminal methyl groups of the two isomers appear as four separated singlets. The separation is better in (D_6)benzene. While the 9,10-ethylenic protons appear as a multiplet (9 lines in first approximation) between 5.51 and 5.96 ppm, the methylidene protons of *trans*- and *cis*-**10** – which are near the epimeric C-atom C(5) – are well separated and resonate as four groups of signals centered at 4.53, 4.70, 4.77 and 4.90 ppm. The signals at 4.70 and 4.90 ppm have triplet character (J = 1.8 and 1.3 Hz) due to ^2J-coupling and ^4J-coupling with H–C(5). The complexity of signals at 4.53 and 4.77 ppm is probably due to additional ^5J-coupling with the bridgehead proton at C(8). As coupling across 5 bonds is generally observed for a rigid, nearly planar W-configuration, the signals at 4.53 and 4.77 ppm are probably due to the transoid methylidene proton, remote from the geminal methyl groups, and the signals at lower field (4.70 and 4.90 ppm) to

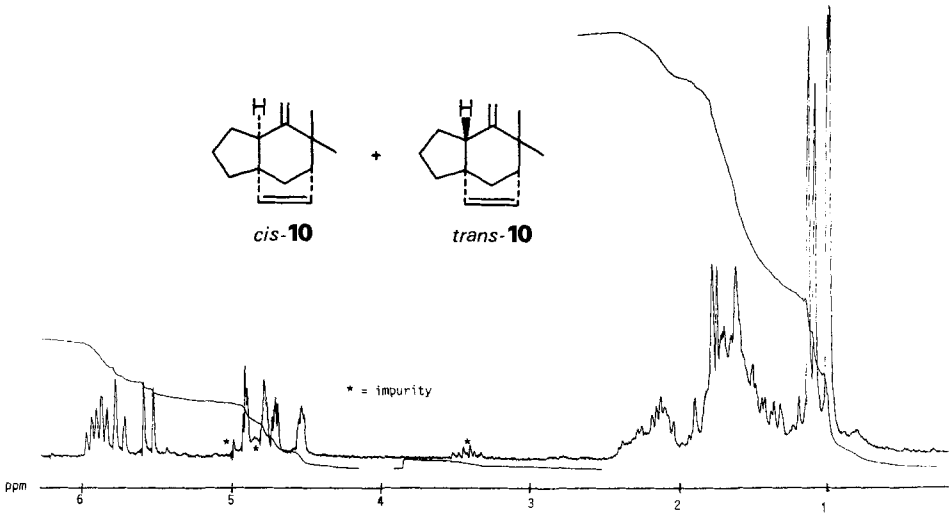


Fig. 1. *90-MHz ^{1}H-NMR. spectrum* ($CDCl_3$, benzene standard)

the cisoid methylidene proton, which suffer *van der Waals* deshielding by the geminal methyl groups[4]). Since previous work on bicyclo[3.2.1]oct-6-enes had shown that α-methyl protons at C(2) and C(4) appeared at higher field than β-methyl protons – anisotropic shielding by the endocyclic double bond [13] – the signals of the methyl groups in *trans*-**10** and *cis*-**10** could be assigned *(Table 1)*. In *cis*-**10** and in its 9,10-hydrogenated derivative **11**, the signals of the geminal methyl protons are further apart than in *trans*-**10** and its 9,10-hydrogenated derivative **1a**. In *cis*-**10** and **11**, the β-methyl group suffers *van der Waals* repulsion and deshielding by the β-oriented methylene group at C(4) of the tricycle, whereas the α-oriented methyl group is in approximately the same environment in both isomers *(cf. Table 1)*.

The splitting pattern of the methylidene protons is simpler in **1a** and **11** than in *trans*- and *cis*-**10**. Hydrogenation of the endocyclic 9,10-double bond should render the tricyclic skeleton more flexible, with concomitant loss of long range coupling, probably caused by the rigidity of **10**.

Table 1. *^{1}H-NMR. chemical shifts* (δ, ppm) *of geminal methyl and methylidene protons*

	1b[a])	**1d**[3])[b])	*cis*-**10**[c])	*trans*-**10**[c])	**11**[b])	**1a**[b])
$C(CH_3)_2$	1.04	1.04	0.97 (α)	0.99 (α)	1.05	1.05
	1.06	1.07	1.12 (β)	1.07 (β)	1.14	1.09
$C{=}CH_2$	4.53	4.61	4.77	4.53	4.79	4.58
	4.68	4.75	4.90	4.70	4.87	4.74

[a]) 60 MHz, CCl_4, TMS; see [4e]. [b]) 90 MHz, $CDCl_3$, TMS. [c]) 90 MHz, $CDCl_3$, benzene.

[3]) We thank Prof. *G. Ohloff* and Dr. *B. Maurer* (Firmenich SA, Geneva) for a sample of natural zizanoic acid **1d**.

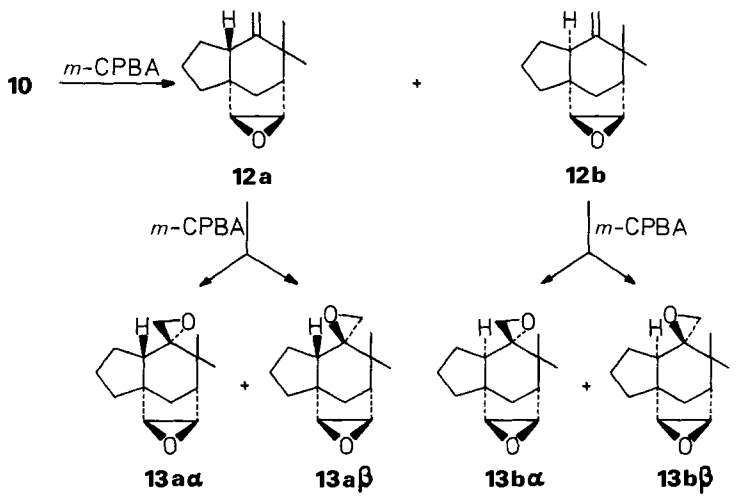
[4]) The opposite ^{1}H-NMR. assignment has been made for the methylidene protons in the ester of **1d**; see [12].

4. Reactions of 9,10-dehydro-2-norzizaene (*10*). – 4.1. *Silver nitrate complexation.* On adding a concentrated solution of *ca.* 1.3 equivalents of $AgNO_3$ in deoxygenated water to neat **10**, a precipitation of a white to pale yellow paste occurred. The complex was unstable at r.t., especially when moist (deliquescence and black coloration), but it could be kept for several weeks at $-20°$ without discernible change. The tricycle could be recovered quantitatively by treating the dried paste with moist ether or pentane. The isomeric ratio *cis*-**10**/*trans*-**10** after cleavage of the complex was identical to the ratio before complexation, *i.e.* selective complexation of one isomer by silver ion was not observed.

4.2. *Hydrogenation and epoxidation.* Hydrogenation of **10** with diazene readily gave 2-norzizaene **1a**+**11**. Attack of the methylidene group was not observed. In contrast, epoxidation of **10** with *m*-chloroperbenzoic acid (*m*-CPBA, 1.8 equiv.) was not selective and gave two monoepoxides (24%) and four diepoxides (76%). On the assumption that the endocyclic 9,10-double bond of *trans*- and *cis*-**10** is attacked from the *exo*-side only and that the methylidene group is attacked from both *α*- and *β*-sides *(Scheme 7)*, two monoepoxides **12a** and **12b** and four diepoxides **13aα**, **13aβ** (from **12a**) and **13bα** and **13bβ** (from **12b**) are possible. In the ^{1}H-NMR. spectrum of the mixture, the cyclopentenoid ethylenic protons had completely disappeared, whereas the signals of methylidene protons were still present at reduced intensity. Hence the cyclopentenoid double bond was epoxidized preferentially.

In another experiment **10** was epoxidized with a smaller excess (1.3 equiv.) of *m*-CPBA, which was added in small portions to **10**. After 2 h only one monoepoxide and two diepoxides in a ratio 3.6:1:1 were observed, 5% of tricyclic **10** remaining. In the ^{1}H-NMR. spectrum again no cyclopentenoid protons were present, but in the region of the methylidene protons two double doublets at 4.63 and 4.80 ppm (90 MHz, $CDCl_3$) were discernible, which, on the basis of the assign-

Scheme 7. *Epoxidation of 9,10-dehydro-2-norzizaene* (**10**)



ments of hydrocarbons **10** and **1a** + **11**, were ascribed to a monoepoxide with *trans*-perhydroindan structure, *i.e.* **12a**. Hence, monoepoxide **12b** derived from *cis*-perhydroindan *cis*-**10** seems to afford diepoxides more readily – even in the presence of *cis*-**10** + *trans*-**10** – than monoepoxide **12a** derived from *trans*-perhydroindan *trans*-**10**[5]). Epoxidation of the isomeric monohydrogenated tricyclics **1a** and **11** with a deficiency of *m*-CPBA (0.5 equiv.) showed also that *cis*-perhydroindan **11** reacted preferentially, the ratio **11**:**1a** dropping from 1:1.29 before epoxidation to 1:2.25 after partial epoxidation. The mixture of epoxides had a beautifully fresh herbaceous odour, reminiscent of valuable conifers and of aspects of vetiver oil[6]).

5. Conclusion. – With the preparation of **10** from **8** by 'chromatographic cycloaddition' at $\leqslant -30°$, the methodology for generating and capturing highly alkylated carbocations which are easily deprotonated, has been developed further. The new route to functionalized tricyclo[6.2.1.$0^{1,5}$]undec-9-enes is short and flexible. The strained C(9), C(10)-double bond is useful for *(i)* providing a site for π-complexation, *e.g.* by $AgNO_3$, which allows easy separation, purification and storage of oily **10**; *(ii)* introducing strain, which holds the labile methylidene double bond in the *exo*-position without isomerization; *(iii)* allowing access to new analogues of zizaene – for instance with novel oxygen substitution – which have not yet been encountered in any natural products.

We thank the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for support of our work.

Experimental Part

General remarks. ^{1}H-NMR. spectra (ppm, J Hz) were recorded in $CDCl_3$, unless otherwise specified. TMS served as internal standard except for the 90 MHz spectra of the silylated compounds; in this case benzene was used ($\delta = 7.26$ ppm). 60 MHz spectra of silylated compounds were recorded initially without a standard and then with added TMS. ^{13}C-NMR. spectra were recorded in $CDCl_3$ ($\delta = 77.0$ ppm). Mass spectra (m/z) were measured on *Varian CH-5* and *MAT 312* spectrometers at r.t. Microanalyses were carried out by Mrs. *E. Jirotka,* Department of Organic Chemistry, University of Hannover.

Preparation of 4-chlorobutanal. Oxidation of 4-chlorobutanol (10.8 g, 0.1 mol) with pyridinium chlorochromate (32.2 g, 0.15 mol) in dry CH_2Cl_2 (200 ml) gave 5.1 g (48%) of 4-chlorobutanal, b.p. 45–48°/14 Torr. It was stored under N_2 at $-20°$ because of ready oxidation. – IR. (film): 2835*w*, 2730*w*, 1723*s* (C=O). – ^{1}H-NMR. (60 MHz): 2.11 (*qi*, $J = 6.5$, 2 H, $CH_2CH_2CH_2$); 2.70 (*t*, $J = 6.5$, 2 H, CH_2CHO); 3.64 (*t*, $J = 6.5$, 2 H, CH_2Cl); 9.91 (*s*, 1 H, CHO).

Preparation of ethyl 6-chloro-2(trimethylsilyl)methyl-2-hexenoate (**6**). Ethyl (diethylphosphono)-acetate (20 g, 17.9 ml, 89.4 mmol) in dry DME (25 ml) was deprotonated with 75% NaH (3 g, 93.7 mmol), which had previously been suspended in dry DME (60 ml). After reaction with iodomethyl(trimethyl)-silane (21.1 g, 98.5 mmol) in DME (40 ml) for 3 h at 70°, deprotonation was repeated with 75% NaH

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[5]) Preliminary experiments with *t*-BuOOH/$Mo(CO)_6$ [14], indicate a more selective epoxidation, with formation of two diepoxides instead of four.

[6]) We thank Dr. *E.J. Brunke*, Dragoco, for having carried out the sensory evaluation.

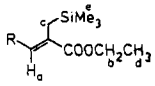
[7]) We thank Dr. *F.J. Hammerschmidt,* Dragoco, Holzminden, for the GC./MS. measurements.

(3 g, 93.7 mmol). Finally, a solution of 4-chlorobutanal (10 g, 93.8 mmol) in DME (15 ml) was added at 0° and the resulting stirred milky grey-yellow mixture was allowed to reach r.t. overnight. It was poured carefully into water (450 ml), the aqueous solution was extracted with ether (4 × 75 ml), the combined organic phase was washed with dil. NaCl-solution (70 ml) until neutral, dried ($MgSO_4$) and evaporated at 20–30° at reduced pressure. The residue was fractionated by bulb distillation. The fraction collected (*ca.* 11 g) at 115–140° (bath temp.)/*ca.* 1 Torr was chromatographed on silica gel (light petroleum/ethyl acetate 10:1) and gave pure **6** (7.1 g, 30%) as a colourless to pale yellow oil. A small amount of the (*E*)-isomer of **6** was discernible in the crude product, but was separated after chromatography. – IR. (CCl_4): 3023*m* (CH=), 1712*vs* (C=O), 1639*m* (C=C), 1218*vs*, 854*vs*, 670*s*. – ^{1}H-NMR. (90 MHz): −0.08 (*s*, 9 H, $SiMe_3$); 1.19 (*t*, *J* = 7, 3 H, OCH_2CH_3); 1.62–1.95 (*m*, 2 H, $CH_2CH_2CH_2$); 1.74 (br. *s*, 2 H, CH_2Si); 2.03–2.30 (*m*, 2 H, CH_2CH=); 3.44 (*t*, *J* = 6, 2 H, CH_2Cl); 4.07 (*qa*, *J* = 7, 2 H, OCH_2); 6.45 (br. *t*, *J* = 7, 1 H, CH=). – ^{13}C-NMR.: −1.21 (*qa*, $SiMe_3$); 14.12 (*qa*, CH_2CH_3); 17.33 (*t*, CH_2Si); 26.05 (*t*, CH_2CH=); 31.53 (*t*, $CH_2CH_2CH_2$); 44.14 (*t*, CH_2Cl); 60.28 (*t*, CH_2O); 131.55 (*s*, C=); 135.61 (*d*, CH=); 167.84 (*s*, C=O). – MS.: 262 (2, M^+), 247 (12, $M-CH_3$), 227 (6, $M-Cl$), 185 (35), 109 (20), 81 (53), 75 (49), 73 (100, Me_3Si^+), 53 (34), 45 (28).

$C_{12}H_{23}ClO_2Si$ (262.85) Calc. C 54.83 H 8.82% Found C 55.47 H 8.84%

Table 2. *^{1}H-NMR. shifts* (90 MHz, $CDCl_3$, benzene standard) *of*

6a R = H
6b R = CH_3
6 R = $(CH_2)_3Cl$

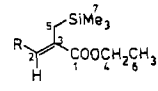


	H_a	H_b	H_c	H_d	H_e	R
						H
6a[a])	5.89	4.09	1.76	1.20	−0.07	5.20
						CH_3
6b[a])	6.64	4.07	1.75	1.19	−0.07	1.63
						$CH_2CH_2CH_2Cl$
6	6.45	4.07	1.74	1.19	−0.08	H_f 2.03–2.30
						H_g 1.62–1.95
						H_h 3.44

[a]) See also [9].

Table 3. *^{13}C-NMR. shifts* (20.15 MHz, $CDCl_3$, benzene standard, δ) *of*

6a R = H
6b R = CH_3
6 R = $(CH_2)_3Cl$



	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	R
6a	166.96	120.71	138.52	60.07	21.93	13.85	−2.15	
								CH_3
6b	167.51	132.01	131.04	59.77	16.57	13.91[a])	−1.48	14.21[a])
								$CH_2CH_2CH_2Cl$
6	167.84	135.61	131.55	60.28	17.33	14.12	−1.21	C(8) 26.05[b])
								C(9) 31.53[b])
								C(10) 44.14

[a]) Assignment exchangeable. [b]) Assignment according to [15].

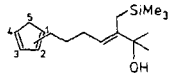
Preparation of 7-chloro-2-methyl-3(trimethylsilyl)methyl-3-hepten-2-ol (**7a**). Compound **6** (6.0 g, 22.8 mmol) in 40 ml of dry ether was allowed to react with a 1.6 M CH_3Li in ether (41 ml, 65.6 mmol) under N_2 at -70 to $-30°$. The solution was stirred for 2 h to reach $-20°$, and ice-cold water (150 ml) was added carefully with cooling. The organic phase was separated, the aqueous phase extracted with ether (2 × 50 ml), the combined organic phases were washed with saturated aqueous NaCl-solution (2 × 25 ml) and dried ($MgSO_4$). After removal of the ether at 20–30°, the crude product was chromatographed (aluminium oxide, activity II–III, *Brockmann;* eluent: light petroleum/ethyl acetate 10:1), giving pure allylic alcohol **7a** (5.14 g, 90%) as a colourless to pale-yellow oil, which was stored at $-20°$. – IR. (CCl_4): 3625*m* (OH), 3500*w* br. (OH), 1250*s*, 1171*s*, 852*vs*. – ^{1}H-NMR. (90 MHz): −0.02 (*s*, 9 H, $SiMe_3$); 1.22 (*s*, 6 H, CMe_2); 1.23 (br., 1 H, OH); 1.56 (br. *s*, 2 H, CH_2Si); 1.59–2.13 (*m*, 4 H, CH_2CH_2CH=); 3.41 (*t*, *J* = 6.5, 2 H, CH_2Cl); 5.15 (*t*, *J* = 6.5, 1 H, CH=). – ^{13}C-NMR.: 0.06 (*qa*, $SiMe_3$); 17.63 (*t*, CH_2Si); 26.02 (*t*, CH_2CH=); 29.84 (*qa*, $C(CH_3)_2$); 32.50 (*t*, $CH_2CH_2CH_2$); 44.47 (*t*, CH_2Cl); 73.24 (*s*, COH); 117.71 (*d*, CH=); 145.85 (*s*, C=). – MS.: 248 (0, M^+), 233 (2, $M-CH_3$), 230 (3, $M-H_2O$), 158 (11), 123 (21), 109 (40), 95 (28), 82 (63), 81 (37), 75 (52), 73 (100, Me_3Si^+), 68 (45), 59 (26), 45 (25), 43 (35), 41 (26).

$C_{12}H_{25}ClOSi$ (248.87) Calc. C 57.91 H 10.13% Found C 57.84 H 10.15%

Preparation of 7-iodo-2-methyl-3(trimethylsilyl)methyl-3-hepten-2-ol (**7b**). Compound **7a** (4.5 g, 18.1 mmol) was added to a solution of dried NaI (5.4 g, 36 mmol) in dry acetone (65 ml). The mixture was refluxed for 48 h, cooled, poured into water (150 ml) and extracted with pentane (4 × 40 ml). The combined organic phases were dried ($MgSO_4$) and the solvent was removed at r.t. under reduced pressure. Chromatography on aluminium oxide (*Brockmann* activity II–III, eluent: light petroleum/ethyl acetate 10:1) gave pure **7b** (5.30 g, 86%) as a pale yellow oil. – IR. (CCl_4): 3623*m* (OH), 1250*s*, 1170*s*, 853*vs*. – ^{1}H-NMR. (90 MHz): −0.02 (*s*, 9 H, $SiMe_3$); 1.22 (*s*, 6 H, CMe_2); 1.24 (br., 1 H, OH); 1.56 (br. *s*, 2 H, CH_2Si); 1.58–2.09 (*m*, 4 H, CH_2CH_2CH=); 3.08 (*t*, *J* = 6.5, 2 H, CH_2I); 5.14 (*t*, *J* = 6.5, 1 H, CH=). – ^{13}C-NMR.: 0.12 (*qa*, $SiMe_3$); 6.48 (*t*, CH_2I); 17.75 (*t*, CH_2Si); 29.57 (*t*, CH_2CH=); 29.84 (*qa*, $C(CH_3)_2$); 33.38 (*t*, $CH_2CH_2CH_2$); 73.21 (*s*, COH); 117.32 (*d*, CH=); 145.85 (*s*, C=). – MS.: 340 (0, M^+), 322 (11, $M-H_2O$), 250 (8, $M-Me_3SiOH$), 123 (47, $M-Me_3SiOH/I$), 95 (35), 81 (45), 75 (33), 73 (100), 67 (21), 43 (18).

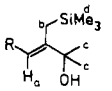
Preparation of 7-(1,3-cyclopentadienyl)-2-methyl-3(trimethylsilyl)methyl-3-hepten-2-ol (**8a** *and* **8b**). The reaction was carried out in two steps: *(i)* neutral aluminium oxide (activity I) (15 g) and small pieces of sodium (1.15 g, 0.05 g-atom) were introduced into a flamedried flask which was heated at *ca.* 5 Torr until all the sodium had melted. The liquid metal was dispersed on the aluminium oxide by stirring and shaking until a homogeneous, grey powder resulted. The contents of the flask were flushed with N_2, cooled to r.t. with vigorous stirring and dry THF (50 ml) was added. The flask was cooled in an ice-bath and cyclopentadiene (4 g, 5 ml, 0.06 mol) was dropped in carefully, the suspension being stirred another 10 min at 0°. After the aluminium oxide had settled, the supernatant colourless solution was used immediately for the next stage (on standing cyclopentadienylsodium assumes a red coloration due to reaction with traces of oxygen).

Table 4. *^{13}C-NMR. chemical shifts of cyclopentadienyl C-atoms in* **8a**, **8b**, *in 1-methylcyclopentadiene* (**14**) *and 2-methylcyclopentadiene* (**15**)



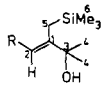
	8a[a])	**8b**[a])	**14**[b])	**15**[b])
C(1)	149.21	125.68	144.6	127.3
C(2)	126.31	146.76	128.4	142.6
C(3)	132.25	134.55	134.1	136.5
C(4)	130.01	133.28	130.7	133.4
C(5)	42.95	40.92	45.0	40.7

[a]) 20.15 MHz, $CDCl_3$, $CDCl_3$ standard. [b]) 25.14 MHz, no solvent, benzene/cyclohexane standard [16].

Table 5. *^{1}H-NMR. of*  (90 MHz, $CDCl_3$, benzene standard)

	H_a	H_b	H_c	H_d	R
					H
16	4.85	1.49	1.24	−0.03	4.52
					CH_3
17	5.32	1.54	1.22	−0.03	1.45
					$\overset{e}{C}H_2\overset{f}{C}H_2\overset{g}{C}H_2Cl$
7a	5.15	1.56	1.22	−0.02	H_e, H_f 1.59–2.13; H_g 3.41
					$CH_2CH_2CH_2I$
7b	5.14	1.56	1.22	−0.02	H_e, H_f 1.58–2.09; H_g 3.08
					$CH_2CH_2CH_2C_5H_5$
8a+9a	5.21	1.51	1.22	−0.05	H_e 1.73–2.01; H_f 1.40–1.69; H_g 2.11–2.44

[a]) See also [9].

Table 6. *^{13}C-NMR. of*  (20.15 MHz, $CDCl_3$, $CDCl_3$ standard)

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	R
16	153.60	106.08	73.34	29.11	20.96	−0.82	
							CH_3
17	145.09	113.20	73.00	29.54	17.03	−0.09	14.12
							$\overset{7}{C}H_2\overset{8}{C}H_2\overset{9}{C}H_2Cl$
7a	145.85	117.71	73.24	29.84	17.63	+0.06	C(7) 26.02[a]); C(8) 32.50[a]); C(9) 44.47
							$CH_2CH_2CH_2I$
7b	145.85	117.32	73.21	29.84	17.75	+0.12	C(7) 29.57[a]); C(8) 33.38[a]); C(9) 6.48
							$CH_2CH_2CH_2C_5H_5$
8a+9a	144.31	119.35	73.03	29.75	17.39	0.00	C(7), C(8), C(9) 28.42–30.23

[a]) Assignment according to [15].

(ii) An aliquot of the solution of cyclopentadienylsodium (38 ml, *ca.* 36 mmol) was injected into a solution of the iodide **7b** (4.5 g, 13.2 mmol) in dry THF (25 ml). The reaction mixture slowly turned brown-yellow, while being stirred for 3 h at 0°. It was poured onto ice/water (200 ml), extracted with ether (4×75 ml) and the combined organic phases were washed with saturated aqueous NaCl-solution (70 ml), dried ($MgSO_4$) and freed from the solvent at r.t. and reduced pressure. The resulting dark-red oil (3.8 g) was chromatographed on silica gel (CH_2Cl_2 or light petroleum/ethyl acetate 10:1) to afford 3.20 g (87%) of a light yellow oil of **8a** and **8b** (ratio 44:56), which was stored as a dilute solution in pentane at −20°. – IR. (CCl_4): 3620*m* (OH), 3480*w* (OH), 3040*w* (CH=), 1648*w* (C=C), 1613*w* (C=C), 1249*s*, 1170*s*, 853*vs*. – ^{1}H-NMR. (90 MHz): −0.05 (*s*, 9 H, $SiMe_3$); 1.22 (*s*, 6 H, CMe_2); 1.27 (*s*, 1 H, OH); 1.40–1.69 (*m*, 2 H, $CH_2CH_2CH_2$); 1.51 (br. *s*, 2 H, CH_2Si); 1.73–2.01 (*m*, 2 H, CH_2CH=); 2.11–2.44 (*m*, 2 H, CH_2cp); 2.77 (*qa*, *J* = 1.5, CH_2 in cp in **8a**); 2.85 (*qa*, *J* = 1, CH_2 in cp in **8b**); 5.21 (*t*, *J* = 6.5, 1 H, CH=); 5.92, 6.08, 6.17, 6.33 (each signal *m*, 3 H altogether, CH= in cp). – ^{13}C-NMR.: 0.00 (*qa*, $SiMe_3$); 17.39 (*t*, CH_2Si); 28.42, 28.51, 28.69, 29.41, 29.54, 30.23 (not resolved, $CH_2CH_2CH_2$ in **8a** and **8b**); 29.75 (not resolved, $C(CH_3)_2$); 40.92 (*t*, CH_2 of cp in **8b**); 42.95 (*t*, CH_2 in cp in **8a**); 73.03 (*s*, COH); 119.35 (*d*, CH=); 125.68, 126.31, 130.01, 132.25, 133.28, 134.55 (each signal *d*, CH= in cp in **8a** and **8b**); 144.31 (*s*, C=); 146.76 (*s*, C= in cp in **8b**); 149.21 (*s*, C= in cp in **8a**). – MS.: 278 (1, M^+), 260 (2, $M-H_2O$), 194 (7), 188 (6), 107 (18), 75 (48), 73 (100), 45 (14).

$C_{17}H_{30}OSi$ (278.51) Calc. C 73.31 H 10.86% Found C 73.31 H 10.76%

Preparation of 7,7-dimethyl-6-methylidenetricyclo[6.2.1.0^{1,5}]undec-9-ene (9,10-dehydro-2-norzizaene) (**10**). – *(i)* A solution of allyl alcohol **8** (1.6 g, 5.74 mmol) in dry CH_2Cl_2 (20 ml), kept under N_2 at −70°, was slowly dropped into a mixture, prepared at −70°, of trifluoroacetic anhydride (1.32 g, 0.89 ml, 6.3 mmol) and ethyldiisopropylamine (0.82 g, 1.09 ml, 6.35 mmol) in dry CH_2Cl_2 (15 ml). The resulting homogeneous yellow-orange solution was stirred for 3 h at −70° and diluted with pre-cooled (−40°) pentane (75 ml) to give the crude trifluoroacetate [IR. ($CHCl_3$): 1775*s* (C=O), 1249*s*, 1170*vs*, 850*vs*] which was passed down a column made up immediately beforehand from neutral aluminium oxide (120 g, activity I) and a suspension of anhydrous $ZnCl_2$ (7 g, 51.3 mmol) in pentane. The column was equipped with a cooling jacket, which was kept at −30° with circulating cooling liquid. The solution was eluted slowly with pentane and the eluate was collected in a flask under exclusion of moisture, while being stirred with K_2CO_3 (*ca.* 3 g) at −20 to 0°. After collection of *ca.* 400 ml of eluate, chromatography was stopped and the solution was filtered and concentrated to *ca.* 40 ml under reduced pressure at 0°. The solution was filtered under slight pressure through a short column of silica in pentane. In this fashion remaining trifluoroacetate was destroyed, recognizable as a deep-violet zone in the upper part of the column. The column was washed with pentane and the combined eluate was evaporated under reduced pressure, yielding a yellow-orange oil (*ca.* 1.3 g), which was bulb-distilled *in vacuo*. Redistillation of the fraction distilled at a bath temperature of 70–100°/*ca.* 2 Torr gave tricyclic **10** (*trans*-**10**/*cis*-**10** = 1.15:1) as a colourless oil which was kept in dilute pentane solution or as $AgNO_3$ complex, stable at −20°. Yield: 0.17 g, 15.7% with respect to **8**, b.p. 75–85°/*ca.* 2 Torr. – ^{1}H-NMR. (90 MHz, $CDCl_3$, benzene standard): 0.97, 0.99, 1.07 and 1.12 (each signal *s*, 6 H altogether, CH_3); 1.28–1.93 (*m*, 8 H, CH_2); 1.95–2.40 (*m*, 2 H, bridgehead-H); 4.53 (*m*); 4.70 (~*t*, *J* = 1.8); 4.77 (*m*); 4.90 (*t*, *J* = 1.3, 2 H altogether, $=CH_2$); 5.51–5.96 (*m*, 2 H, CH=); *cf. Fig. 1.* – GC./MS. (50 m WG 11 capillary column, 4°/min)[7]: *cis*-**10** (*cis*-perhydroindan, shorter GC. retention time): 188 (44, M^+), 173 (73), 159 (13), 145 (82), 131 (32), 118 (80), 105 (30), 91 (100), 79 (48), 77 (51), 67 (29), 53 (20), 41 (32). *trans*-**10** (*trans*-perhydroindan, longer GC. retention time): 188 (54, M^+), 173 (54), 159 (12), 145 (100), 131 (21), 119 (54), 117 (49), 105 (32), 91 (94), 79 (45), 77 (49), 67 (24), 53 (21), 41 (29). – HR./MS.: $C_{14}H_{20}$, Calc. 188.1565, Found 188.1564.

(ii) Cycloaddition promoted by $TiCl_4/C_6H_5NHCH_3$ [11]. A solution of freshly distilled $TiCl_4$ (0.51 g, 0.3 ml, 2.7 mmol) in dry CH_2Cl_2 (18 ml) was cooled to −40° and freshly distilled *N*-methylaniline (0.29 g, 0.29 ml, 2.7 mmol) was added dropwise. The dark-red mixture was stirred for 15 min at −10° under N_2, cooled to −60° and mixed slowly with a solution of allyl alcohol **8** (0.5 g, 1.8 mmol) in dry CH_2Cl_2 (17 ml). The resulting brownish suspension was stirred and allowed to reach −10° during 3 h. It was poured into ether (100 ml), the organic phase was washed with water (3×50 ml), dried ($MgSO_4$) and evaporated at r.t. under reduced pressure. The viscous yellow-orange, oily residue (0.45 g) was taken up in a little pentane and filtered through a short column of silica gel (pentane). After removal of the solvent a colourless oil (*ca.* 0.15 g) remained which was distilled at 75–90°/*ca.* 2 Torr (Kugelrohr) giving 0.021 g (6.2%) of **10** (*trans*-**10**/*cis*-**10** = 1:1.2).

Preparation of 7,7-dimethyl-6-methylidenetricyclo[6.2.1.0^{1,5}]undecane (2-Norzizaene) (**1a**+**11**). Tricycle **10** (0.034 g, 0.18 mmol) and dipotassium azodicarboxylate (0.053 g, 0.27 mmol) were suspended in methanol (2 ml) and a solution of glacial acetic acid (0.033 g, 0.55 mmol) in methanol (2 ml) was slowly added at r.t. The mixture slowly became clear on stirring for 1 h at r.t. It was poured into water (5 ml), the aqueous solution was extracted with pentane (2×5 ml) and the combined organic phases were dried (K_2CO_3). After evaporation under reduced pressure at r.t. hydrogenated tricycle **10** remained as a pale yellow oil (0.033 g, 96%), pure (by GC.). – ^{1}H-NMR. (90 MHz, $CDCl_3$): 1.05 (br. *s*), 1.09 (*s*), 1.14 (*s*) (6 H altogether, CH_3); 1.33–2.37 (*m*, 14 H, $-CH_2-$ and bridgehead-H); 4.58 (*t*, *J* = 1.8); 4.74 (*t*, *J* = 1.8); 4.79 (~ br. *d*, *J* = 1.6); 4.87 (*d*, *J* = 1.6, 2 H altogether, $=CH_2$). – GC./MS.[7]): **11** (*cis*-perhydroindan, shorter GC. retention time): 190 (13, M^+), 175 (23), 162 (10), 147 (34), 133 (20), 121 (47), 120 (100), 119 (85), 105 (34), 91 (58), 79 (56), 67 (26), 55 (15), 41 (24). **1a** (*trans*-perhydroindan, greater GC. retention time): 190 (10, M^+), 175 (14), 161 (6), 147 (27), 133 (12), 121 (58), 120 (100), 119 (63), 105 (20), 91 (41), 79 (43), 67 (20), 55 (13), 41 (14). – HR./MS.: $C_{14}H_{22}$, Calc. 190.1721, Found 190.1721.

Epoxidation of **10** *with* m-*chloroperbenzoic acid.* Tricycle **10** (isomeric ratio *trans*-**10**/*cis*-**10** = 1.05:1) was treated for 3h at r.t. with 1 equiv. of 85% *m*-chloroperbenzoic acid in the two-phase system CH_2Cl_2/aq. $NaHCO_3$-solution. After aqueous workup unreacted **10** was separated by flash chromatography, and a mixture of epoxides **13** was obtained as a colourless oil which in this case did not solidify at −20°. GC./MS.[7]) indicated 2 monoepoxides (71%) (1:1.16) and 4 diepoxides (29%) (1:1.40:3.89:1.88), corresponding to increasing retention time; ratio of all six components 9.3:10.7:1:1.4:3.9:1.9. – MS.: *cis*-epoxide **12b** (shorter retention time): 204 (12, M^+), 189 (16), 161 (40), 147 (85), 135 (37), 133 (100), 119 (59), 107 (54), 105 (58), 95 (45), 91 (94), 79 (45), 77 (54), 67 (43), 41 (50).

Trans-epoxide **12a** (longer retention time): 204 (3, M^+), 189 (8), 161 (25), 147 (100), 145 (32), 133 (53), 119 (50), 105 (58), 91 (67), 79 (43), 77 (38), 41 (32).

Diepoxide I: 220 (0, M^+), 205 (14), 187 (21), 159 (41), 151 (40), 149 (63), 145 (40), 135 (62), 134 (86), 131 (53), 121 (41), 119 (58), 117 (49), 108 (59), 107 (73), 105 (70), 95 (48), 93 (53), 91 (99), 79 (90), 67 (59), 55 (60), 41 (100).

Diepoxide II: 220 (0, M^+), 205 (7), 164 (25), 149 (100), 131 (44), 121 (40), 119 (32), 108 (81), 107 (68), 105 (42), 93 (54), 91 (45), 79 (62), 77 (40), 67 (37), 41 (62).

Diepoxide III: 220 (2, M^+), 205 (8), 173 (24), 159 (30), 149 (73), 131 (78), 121 (61), 117 (44), 108 (39), 107 (83), 105 (61), 95 (51), 93 (48), 91 (100), 79 (71), 77 (62), 67 (43), 55 (41), 41 (70), 39 (43).

Diepoxide IV: 220 (8, M^+), 205 (18), 189 (24), 163 (36), 159 (33), 151 (71), 149 (89), 145 (39), 134 (48), 131 (58), 121 (47), 119 (54), 108 (60), 107 (85), 105 (63), 93 (58), 91 (86), 81 (44), 79 (95), 77 (70), 67 (59), 55 (56), 41 (100).

^{1}H-NMR. of epoxide mixture (90 MHz, $CDCl_3$, TMS): *inter al.* 1.11, 1.17, 1.18, 1.22 (*s* each, CH_3); 2.89 (*d*, *J* = 3.5); 3.06 (*d*, *J* = 3); 3.23 (*d*×*d*, *J* = 7 and 3.5); 3.42 (*d*×*d*, *J* = 12 and 3 (cyclopentene-epoxide)); 4.62 (*m*); 4.79 (*d*×*d*, *J* = 2 and 1); 4.85 (*m*); 4.96 (*t*, *J* = 1.5) ($CH_2=$; methylidene in mono-epoxide).

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