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Nucleophilic Organosilicon Intermediates Turned Electrophilic: (Trimethylsilyl)methyl, Trimethylsilyloxy and also 2-Tetrahydropyranyloxy as Terminators of Cycloadditions of Allyl Cations. A Short Route to Dehydrozizaenes (6-Methylenetricyclo[6.2.1.$0^{1,5}$]-undec-9,10-enes) and Related Tricycles and [3.2.1]-Bicycles.

H.M.R. Hoffmann*, Ulrike Eggert, Uwe Gibbels, Kunibert Giesel, Oskar Koch, Reinhard Lies, and Jürgen Rabe

Department of Organic Chemistry, University of Hannover, Schneiderberg 1 B, D-3000 Hannover, Federal Republic of Germany

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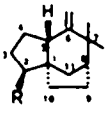
Summary: A range of suitable precursors were synthesized in order to contrast and use Me_3SiCH_2-, Me_3SiO- and THPO-groups as terminators in both inter- and intramolecular cycloadditions of allyl cations to cyclic 1,3-dienes. A variety of crowded bicyclic, tricyclic, and spirofused adducts with [3.2.1]skeletons were obtained. The compounds are of interest, e.g., in perfumery. The work contributes to the development of carbocation-induced cyclization methodology.

In 1976, Fleming, Pearce and Snowden[1a] reported the use of an allylsilane terminator in an intramolecular electrophilic cyclization. This paper, and subsequent work by Fleming and a review,[1b] set the stage for much of the synthetic activity in allylsilane chemistry and general organosilicon chemistry that was to follow.

As yet, allylsilanes have been used infrequently as terminators for intermolecular cycloadditions.[2] Our principal synthetic target was zizaene (1) and some of its structural analogues.[3]



1a	R = H	**1d**	R = CO_2H
1b	R = CH_3	**1e**	R,H = O
1c	R = CH_2OH	**1f**	R,H = CH_2

The synthesis of **1** is a challenge because **1** contains a tricyclic skeleton with (i) a 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 (iii) a crowded exo-methylene bond which tends to shift into 5,6-position under thermodynamic conditions.

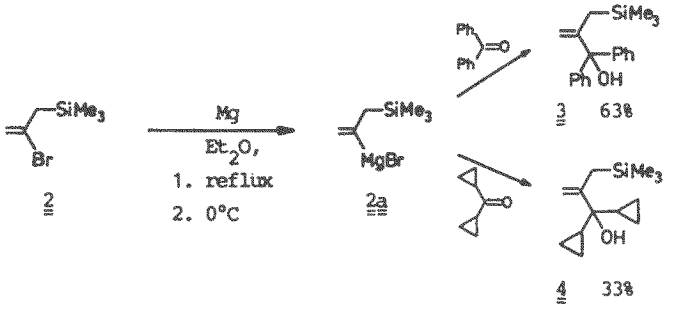
Intermolecular Model Studies. Using the cycloaddition approach (Scheme 1) for the construction of the methylenecyclohexane moiety, we had the chance to study $-CH_2SiMe_3$ as a terminator first in intermolecular, and then also in intramolecular, reactions. In an intermolecular cycloaddition (Scheme 1), two new σ bonds are made and these reactions are therefore expected to be experimentally more demanding than simple intramolecular cyclizations, in which only one new σ bond is formed.

The work allowed us to compare the $-CH_2SiMe_3$ terminator with oxa-analogs, i.e. $-OSiMe_3$ and -OTHP groups, and it also led to a variety of novel structures with interesting properties.

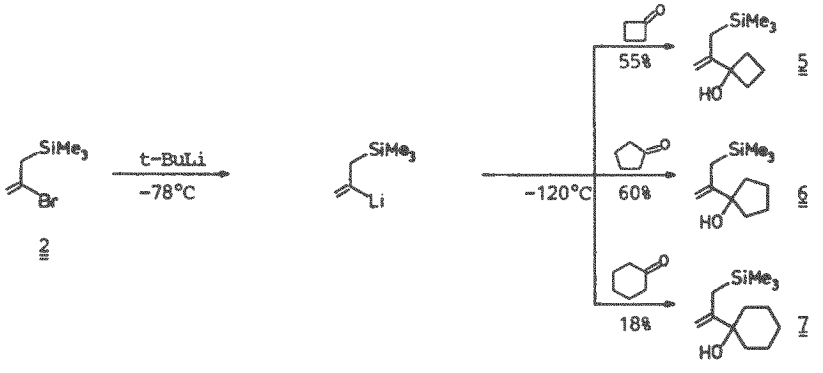
Scheme 1

First of all, a range of 2-[(trimethylsilyl)methyl]allyl alcohols were required. We used two routes, (i) the electrophilic capture of silylated vinyl anions with carbonyl compounds (Scheme 2a & 2b) and (ii) the reaction of appropriately functionalized acrylic esters with di-Grignard reagents (Scheme 3). The vinylmagnesium route was used for carbonyl components which could not enolize, whereas the vinyllithium intermediate generated by metal halogen exchange (Scheme 2b) allowed the capture of carbonyl compounds at low temperature. Thus, the undesired enolization of the carbonyl component was minimized.

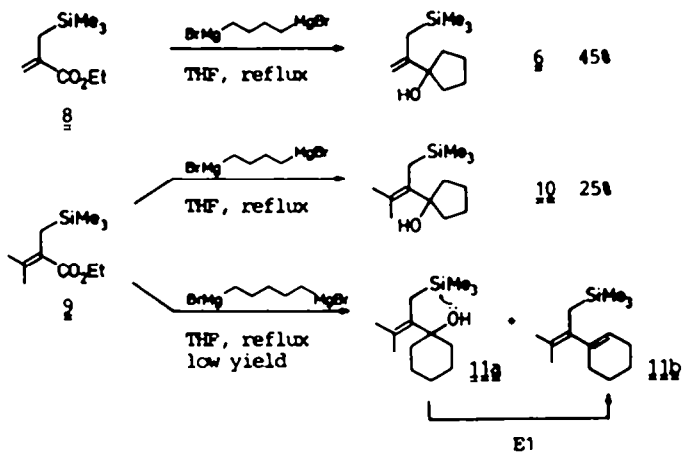
Scheme 2a Vinyl Grignard Reagent.



Scheme 2b Vinyllithium Reagent via Metal-halogen Interchange.



Scheme 3 Cyclizing Grignard Reaction of Silylated Acrylic Esters.



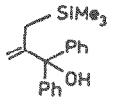
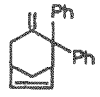
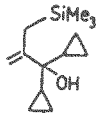
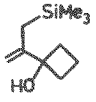
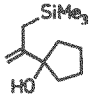
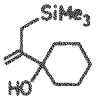
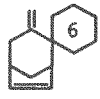
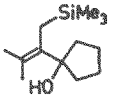
Di-Grignard reagents are well known to react with esters to form tertiary alcohols.[4] Indeed, reaction of the functionalized acrylic esters 8 and 9 with the 1,4-butane di-magnesium reagent gave 6 and 10, respectively. Formation of the tertiary cyclopentanols was relatively smooth, both in the vinyllithium series and via the Grignard cyclization reaction. In contrast, preparation of cyclohexanol derivatives such as 7 and 11a was more difficult. Alcohol 11a, obtained via the double Grignard reaction, is also a tetrasubstituted alkene which was not isolated in pure form. Apparently, the multiply-activated tertiary alcohol suffers ready loss of water which is facilitated by intramolecular electrophilic assistance of silicon (11a → 11b).

Generally, the preparation of allylic alcohols having tetrasubstituted double bonds such as 10 and also bearing OTHP-groups, e.g. 19 below, was more difficult than preparation of allylic alcohols with a simple methylene terminus, e.g. 3, 5, and 6. Clearly, the vinylmetals used as intermediates are destabilized by additional alkyl groups.

With allylic alcohol 3 - 10 at hand we could test the approach delineated in Scheme 1. We had shown earlier that functionalized allyl alcohols can be activated via conversion into trifluoroacetates and treatment with zinc halide.[3,5] A simpler method of an S_N1-type activation is the reaction with $TiCl_4$/N-methylaniline at -20°C in CH_2Cl_2.[6]

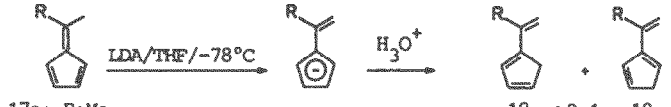
As expected the reactions of the structurally and electronically unbalanced allyl cation precursors 3 - 7 with cyclopentadiene gave cycloadducts 12 - 15 in modest yields (Table 1). In fact, it is interesting that 12 and 13 were formed at all, because it was by no means clear at the outset wether one allylic cation terminus would be overstabilized at the expense of the other. This problem could have jeopardized the formation of two σ bonds. The cycloaddition was more effective starting with the tetrasubstituted precursor 10, giving 16 in 58% yield. Tetracycle 13 is a new sesquiterpenoid ($C_{15}H_{20}$) and so is the tricyclic spiroannulated adduct 16 ($C_{15}H_{22}$) which is also structurally closely related to dehydrozizaene and has a strong smell of pepper. The unsaturated tricycle 14 has a smell of mint.

Table 1 Intermolecular Cycloadditions with Cyclopentadiene/$TiCl_4$/PhNHMe.

3		12		21%
4		13	 sesquiterpenoid	20%
5			no cycloadduct	
6		14		25%, 43%
7		15		15%
10		16	 sesquiterpenoid	58%

Cycloadditions of Vinylcyclopentadienes. $-CH_2SiMe_3$ and $-OSiMe_3$ as Terminator. Recently, a variety of vinylcyclopentadienes 18/19 have been prepared for the first time. Low temperature deprotonation of fulvenes 17 and quenching with dilute acid was successful (Scheme 4). The trienes 18/19 have already been used in intramolecular Diels-Alder reactions[7a] and they were now tested as potential precursors of bridged methylenecyclohexane derivatives.

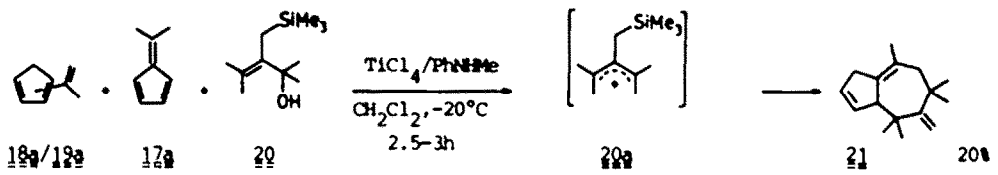
Scheme 4



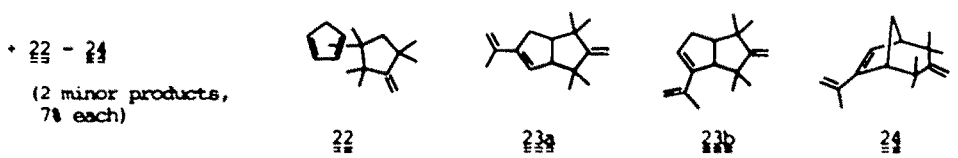
17a: R=Me 18 ∿2:1 19

Intermolecular reactions of the tautomeric mixture of vinylcyclopentadienes and fulvenes (18a : 19a : 17a = 6 : 3 : 1) gave only one clearly identifiable [4 + 3] adduct 21 and two minor adducts: One was probably the [3 + 2] adduct 22, present as a mixture of 1- and 2-substituted valence tautomers. The other was either a [3 + 2] adduct 23a/b or 24 (Scheme 5).[7b]

Scheme 5



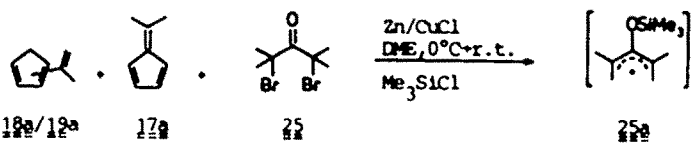
18a/19a 17a 20 20a 21



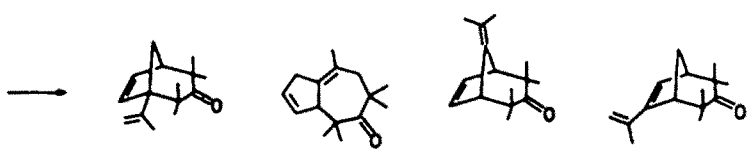
22 23a 23b 24

In contrast, cycloaddition using the more nucleophilic $-OSiMe_3$ terminator (25 → 25a) afforded 7-membered ring adducts 26 and 27 as the major products which were present in a ratio of 1 : 1 (Scheme 6). A minor product 28 was derived from 6,6-dimethylfulvene (17a). Further minor products could be recognized by GC, but could not be isolated in substance. There were no indications for the formation of 29 in significant amounts (it is not clear wether 29, if formed, would have survived the Lewis-acidic reaction conditions). Bicycles 26, 27, and 28 are new sesquiterpenoids ($C_{15}H_{22}O$).

Scheme 6



18a/19a 17a 25 25a



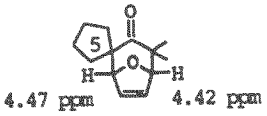
26 12% 27 12% 28 3% 29 (?)

The reactions in both Schemes 5 and 6 involve permethylated allyl cations, i.e. 20a and 25a, which have comparable steric demands. Hence, the terminator must be important. Whereas $-CH_2SiMe_3$ is a σ-donor, $-OSiMe_3$ can also function as a nucleophile interacting through space and giving rise to the twisted allyl cation 25b.[5b]

25a 25b

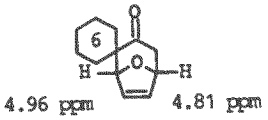
Thus, silylsubstituted cation 20a is the stronger electrophile. The formation of [3.3.0] bicyclics, or five-membered rings in general, with increasing electrophilicity of the allyl cation has been observed in other studies[8], especially by Noyori[8a] and also by us.[9] A comparison of the properties and yields of functionalized methylenecyclohexanes with those of functionalized ketones (cf. Table 2) is instructive. The cycloadducts were prepared via the α,α-dibromo ketone method in the presence of Me_3SiCl (cf. Scheme 6); 30 - 32 and 36, 37 were obtained by ultrasonic activation.[10] In general, the yields of bridged 7-membered ketones are higher than those of the methylene analogues, i.e. $-OSiMe_3$ is more efficient than $-CH_2SiMe_3$ for terminating the formation of the bridged 7-membered ring.

Table 2 Deshielding of Bridgehead Proton by van der Waals Repulsion with Spiroannulated Cyclohexanes (δ, ppm, $CDCl_3$). Steric Stress Revealed.



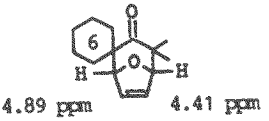
4.47 ppm 4.42 ppm

30
(38%)



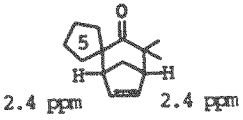
4.96 ppm 4.81 ppm

31
(18%)



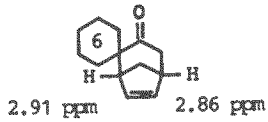
4.89 ppm 4.41 ppm

32
(43%)



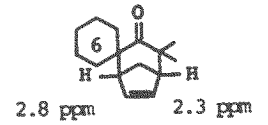
2.4 ppm 2.4 ppm

33
(60%)



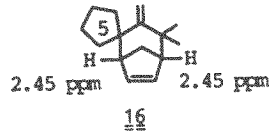
2.91 ppm 2.86 ppm

34
(55%)



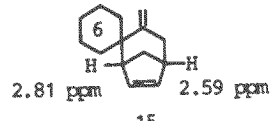
2.8 ppm 2.3 ppm

35
(55%)



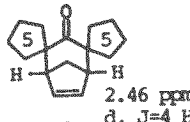
2.45 ppm 2.45 ppm

16
(58%)



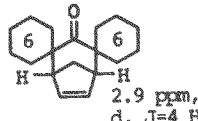
2.81 ppm 2.59 ppm

15
(15%)



2.46 ppm, d, J=4 Hz

36
(71%)



2.9 ppm, d, J=4 Hz

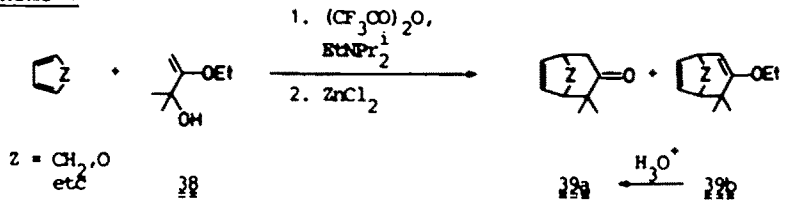
37
(78%,26%)[10]

Adducts 31, 32, 34, 35, 15 and 37 have a spirofused cyclohexane moiety in common. Steric repulsion of this ring with the neighbouring bridgehead proton results in a clear downfield shift of the bridgehead proton. The chemical shift difference of the two bridgehead protons is greater for the gem-dimethylated adducts than for the CH_2 analogues (cf. 32 & 31, 35 & 34). Apparently, the gem-dimethyl groups introduce additional steric stress. A five-membered ring (cf. 30, 33, 16, and 36) exerts no comparable steric pressure on the bridgehead protons, as judged from the ^{1}H NMR signals. Tricycles 30 - 32 have a sweet candy type flavour.

For intramolecular cycloadditions, the α,α-dibromo ketone route is difficult to implement because of the difficulty of preparing suitable precursors; thus, attaching a dibromo ketone moiety to a cyclopentadiene, either directly or by a chain, is not feasible.

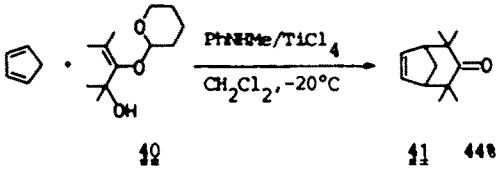
However, previous work showed that allylic alcohol 38 can be activated to form bicyclic ketone 39a and also bicyclic enol ether 39b (Scheme 7).[5a]

Scheme 7



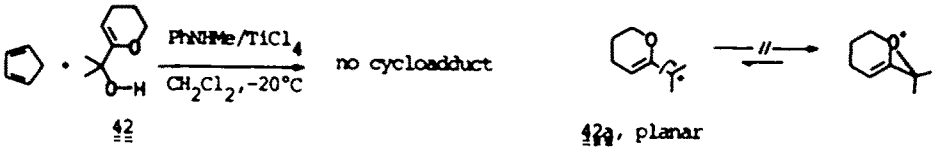
We have now found that the ethoxy group can be replaced by the 2-tetrahydropyranyloxy (-OTHP) group. For instance, cyclopentadiene and 40 gave 41 (Scheme 8), and many further cycloadditions with an OTHP-terminator have been realized.[5c,d]

Scheme 8



However, various attempts to use the structurally related cyclic vinyl ether 42 were not successful (Scheme 9).

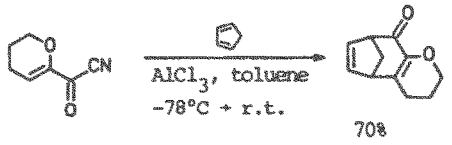
Scheme 9



We surmise that twisting of an intermediate planar allyl cation 42a would do little transfer positive charge onto the inbuilt nucleophilic oxygen, in contrast to 25a ⇌ 25b. Thus, a certain degree of conformational mobility of the

crowded allyl cation seems important for obtaining a crowded cycloadduct.[*] In fact, the only [4 + 3] cycloadditions of an allyl cation comparable with 42a were observed for an α,β-unsaturated acyl cyanide, where E1-type reactions are disfavoured (Scheme 10).

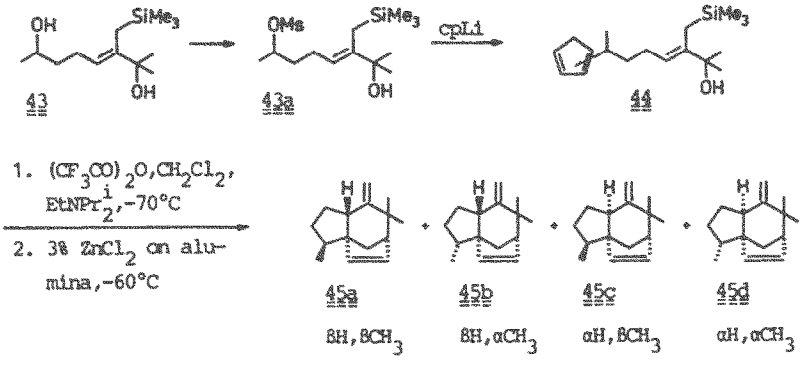
Scheme 10



In the reactions with $AlCl_3$,[11] as in other cases, it is important to use rigorously anhydrous materials and flame-dried apparatus.

Intramolecular Cycloadditions. The stage was now set for intramolecular cycloadditions leading to the zizaene skeleton. Accordingly, 43 was converted selectively into secondary mesylate 43a and coupled with cyclopentadienyl anion (Scheme 11). The tricyclization of the trifluoroacetate of 44 was carried out in a fixed-bed reaction with $ZnCl_2$ on alumina. In this fashion, the products were simultaneously purified by chromatography.

Scheme 11



Starting from 0.7 g of allylic alcohol 44 we obtained 78 mg of 9,10-dehydrozizaenes 45. This corresponds to a yield of 16% or, referring to the reacting 1-substituted valence tautomer of cyclopentadiene, 30%. The direct activation of

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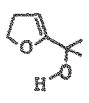
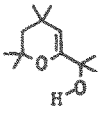
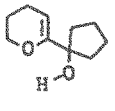
[*] Three other allylic alcohols related to 42 were prepared and tested without success for [4 + 3] cycloadditions. The comparatively intense peak of the molecular ion in the MS could be a pointer to the instability of any derived orthogonal allyl cations and to intramolecular hydrogen bonding (R. Lies, PhD thesis, University of Hannover, 1987).

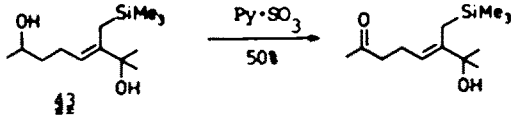




	42		
MS	128 (M^+,19), 113 (25)	142 (M^+,14), 127 (41)	198 (M^+,11), 183 (35)	168 (M^+,53), 150 (30)

alcohol 44 with $TiCl_4$/PhNHMe was preparatively simpler, but gave products which were somewhat less pure.

After the model experiments with vinylcyclopentadienes summarized in Scheme 5, it took some courage to attempt an intramolecular variant of this reaction. Nevertheless, we decided to prepare 46 and obtained it, after difficulties with the oxidation of a secondary alcohol bearing the sensitive tertiary allyl alcohol-allylsilane moiety, had been overcome.[7] Of the various oxidizing agents tried, only py·SO_3 was successful (Scheme 12).

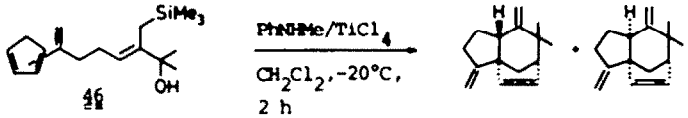
Scheme 12



43

Since conformational mobility of the external chain in 46 should decrease π overlap of the triene portion of the molecule, we speculated that the periselectivity of a cycloaddition should also be modified. After allowing alcohol 46 to react with equimolar $TiCl_4$/PhNHMe, we were pleased to find that the novel bisdehydrozizaenes 47a,b ($C_{15}H_{20}$) had been formed in 20% yield (47a : 47b = 1 : 1). Thus, the intermolecular "model" reactions are unfavourable here and are a poor guide for the actual target, which is constructed intramolecularly.

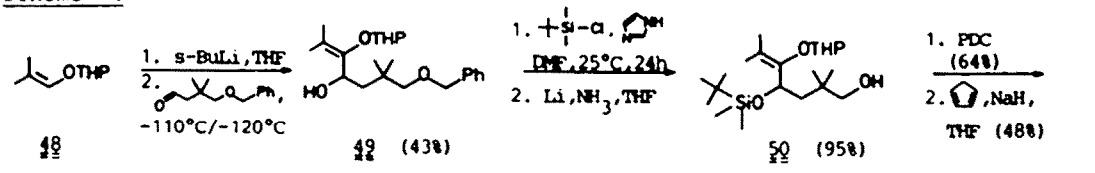
Scheme 13



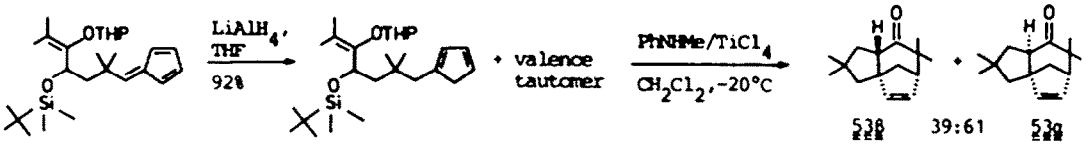
46 47b 47a

The 2-Tetrahydropyranyloxy (-OTHP) Terminator. Since the geminal-dimethyl effect (Thorpe-Ingold effect) facilitates cyclizations and increases yields, we prepared t-butyldimethylsilyl ether 52 (Scheme 14).

Scheme 14



48 49 (43%) 50 (95%)



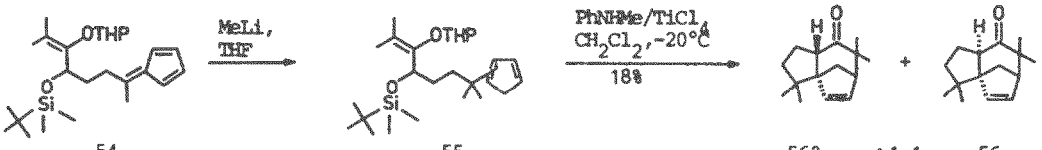
51 52 53b 39:61 53a

At equilibrium: 54:46

30% w.r.t. 52

Cyclization proceeded smoothly (30%) and gave 53α,β, a novel sesquiterpenoid structure. Similarly, intramolecular cyclization of 55 furnished 56 (Scheme 15). In this case, the reaction gave also two isomers of unknown structure. The additional gem-dimethyl group in 53 and 56 facilitated handling and spectroscopic identification of the tricyclics. It is of interest that, at equilibrium, the trans isomer 53β with the natural trans-perhydroindanone stereochemistry predominates 53α.

Scheme 15



54 55 56β ~1:1 56α

+ two unknown isomers[5c]

The role of the OTHP-group is twofold. Firstly, as has been suggested to us by Schlosser,[12] this group is necessary as a handle for the "ortho-lithiation" of a terminally dialkylated enol ether such as 48 (cf. also the preparation of 40 and 54). In other words, fully alkylated vinyllithiums, unlike the simple parent compound, are prone to proton shifts and are much more difficult to handle and to capture by electrophiles. As usual, one must add the carbonyl compound very slowly at as low a temperature as possible in order to minimize enolization. Secondly, the OTHP-group terminates the cycloaddition (cf. also Scheme 7 & 8) and drops off at the latest on acidic work up of the reaction mixture.

We have been criticized for modest yields in previous work on intramolecular cycloadditions.[13] It must not be forgotten that (i) cyclopentadienyl intermediates, unlike those derived from furan, are susceptible to facile 1,5-hydrogen shifts and self-dimerization, (ii) our products are formed convergently in only a few steps in good overall yield, and (iii) strained and crowded tricyclics such as 47, 53 and 57, containing an internal C=C double bond are new and are not accessible by other methods.

Conclusions. α,α'-Dibromo ketones continue to be useful as precursors of allyl cations. In the presence of Me_3SiCl and zinc-copper couple, a 2-silyloxyallyl species is generated which is more electrophilic than that from zinc-copper couple alone and, even more so, from NaI/Cu. For preparing sterically demanding systems such as the dispirofused adducts 36 and 37, ultrasonic activation[10] in addition to Me_3SiCl seems mandatory. The preparation of second- and third-generation allyl cation precursors derived from allylsilanes and enol ethers has allowed us to realize intramolecular cycloadditions and to obtain zizaene and various analogues and to develop new synthetic flexibility in the area of carbocation-promoted cyclizations. Extraordinarily crowded ketones such as 37 (Table 2) are readily accessible and, to our knowledge, they represent the most highly hindered carbonyl compounds known at present. A similar case can be made for bridged methylenecyclohexanes, e.g. 16, which cannot easily be prepared from 33 by current olefination methods and which illustrate the high driving force of the various cyclizations. In essence, 16 and 37 and related sterically encumbered ring systems[9] owe their existence to nucleophilic organosilicon intermediates turned electrophilic.

Acknowledgements. We thank Dr. C. Weiske, Berlin, for advice on nomenclature and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support of our work.

EXPERIMENTAL

Preparation of Allylsilane Precursors. Electrophilic Capture of Vinyl Grignard Reagent (20) to Tertiary Alcohols 3 and 4. To a suspension of Mg (0.187 g, 7.8 mmol) in abs. Et_2O (5 mL) containing catalytic iodine was added 2-bromo-3-trimethylsilyl-1-propene (2)[14] (1.54 g, 8 mmol) in abs. Et_2O (5 mL) under N_2. The suspension was refluxed for 0.5 h until the Mg had dissolved and then the mixture was cooled to 0°C. The ketone (benzophenone for 3, dicyclopropylketone for 4) (7.8 mmol) in abs. ether (10 mL) was added dropwise and the mixture was stirred for 1 h at 35°C. It was then recooled to 0°C and hydrolysed with saturated aqueous NH_4Cl. The organic phase was separated, and the aqueous phase was extracted with ether (3 x 20 mL). The combined ether layer was dried and the solvent was evaporated. On attempted chromatography (Al_2O_3, basic or neutral) the resulting tertiary alcohols decomposed. Therefore, the more volatile educts were removed by Kugelrohr distillation (50°C, 0.1 Torr).

1,1-Diphenyl-2-(trimethylsilyl)methyl-2-propen-1-ol (3). Yield 1.4 g, 63%. IR (CCl_4) 3620 s, 3580 m, 2960 vs, 1250 vs, 1025 vs, cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.04 (s, 9 H, Me_3Si), 1.59 (d, J = 1 Hz, 2 H), 2.45 (br s, 1 H, OH), 4.51 (d, J = 1 Hz, 1 H, olefin. H), 4.93 - 5.0 (m, 1 H, olefin. H), 6.06 - 6.43 (m, 1 OH, Ph-H). MS (70 eV, rt), m/z (rel. intensity) 296 (M^+, 1), 278 (4), 263 (2), 255 (2), 206 (39), 191 (26), 183 (28), 165 (13), 152 (4), 128 (12), 115 (6), 105 (56), 91 (26), 77 (31), 75 (36), 73 (100). Exact mass calcd. for $C_{19}H_{24}OSi$ m/z 296.1596; found 296.1552.

1,1-Dicyclopropyl-2-(trimethylsilyl)methyl-2-propen-1-ol (4). Yield 0.57 g, 33%. IR (CCl_4) 3620 m, 3095 m, 2960 s, 1630 m, 1250 vs, cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.05 (s, 9 H, Me_3Si), 0.24 - 0.61 (m, 8 H, CH_2, cyclopropane), 0.78 - 1.26 (m, 3 H, CH of cyclopropane and OH), 1.66 (d, J = 1.5 Hz, 2 H, CH_2Si), 4.63 - 4.7 (m, 1 H, olefin. H), 5.03 (m, J = 1.5 Hz, olefin. H).MS (70 eV, rt) m/z (rel. intensity) 224 (M^+, 2), 206 (3), 183 (6), 167 (7), 134 (13), 119 (15), 112 (38), 91 (28), 75 (100), 69 (26).

Electrophilic Capture of Vinyllithium Reagent Generated by Metal-Halogen Interchange. 2-Bromo-3-trimethylsilyl-1-propene[14] (2) (1.5 g, 7.8 mmol) was dissolved in a mixture of abs. THF (16 mL), pentane (4 mL) and ether (4 mL) under N_2 and cooled to -78°C. A solution of t-butyllithium in hexane (1.5 molar, 7.8 mL; 11.7 mmol) was added dropwise and the resulting mixture was stirred for 1 h and cooled to -120°C. The ketone (8.6 mmol) was precooled to -78°C and added by syringe at once. The reaction mixture was stirred for 30 min and hydrolysed after removal of the cooling bath. The precipitate formed was dissolved in aqueous NH_4Cl and the product was worked up by chromatography on alumina and by removing volatile educts by Kugelrohr distillation (50°C, 0.1 Torr).

1-[1'-(Trimethylsilyl)methyl-ethenyl]cyclobutanol (5). Yield 0.78 g, 55%. IR (CCl_4) 3620 m, 3480 br w, 2960 vs, 1250 vs, 1145 s, cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.06 (s, 9 H, $SiMe_3$), 1.56 (d, J = 1 Hz, 2 H, CH_2Si), 1.59 - 2.48 (m, 7 H, ring H and 1 OH), 4.67 - 4.74 (m, 1 H, olefin. H), 4.94 (d, J = 1 Hz, olefin. H). MS (70 eV, rt) m/z (rel. intensity) 184 (M^+, 2), 169 (28), 147 (6), 141 (9), 128 (10), 95 (17), 93 (13), 91 (13), 86 (17), 75 (58), 73 (100).

1-[1'-(Trimethylsilyl)methyl-ethenyl]cyclopentanol (6). Yield 0.27 g, 60%. IR (CCl_4) 3600 w, 3480 w, 2960 vs, 1635 vs, 1250 vs, cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.05 (s, 9 H, $SiMe_3$), 1.52 (d, J = 1 Hz, 2 H, CH_2Si), 1.6 - 2.02 (m, 8 H, cyclopentane), 2.23 (br s, 1 H, OH), 4.61 - 4.69 (m, 1 H, olefin. H), 5.0 (d, J = 1 Hz, olefin. H). ^{13}C NMR ($CDCl_3$) δ -0.65 s, 21.8 t, 23.8 t, 38.8 t, 84.4 t, 106.8 t, 151.6 s. MS (70 eV, rt) m/z (rel. intensity) 198 (M^+, 2), 180 (3), 176 (5), 150 (16), 108 (35), 93 (100), 90 (28), 80 (80), 75 (89), 73 (85).

1-[1'-(Trimethylsilyl)methyl-ethenyl]cyclohexanol (7). Yield 0.20 g, 18%. IR (CCl_4) 3520 br w, 2940 vs, 1630 m, 1255 s, cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.05 (s, 9 H, $SiMe_3$), 1.14 - 1.84 (m, 13 H, cyclohexane, CH_2Si and OH), 4.6 - 4.67 (m, 1 H, olefin. H), 4.95 (d, J = 1.5 Hz, olefin. H). MS (70 eV, rt) m/z (rel. intensity) 212 (M^+,2), 194 (4), 179 (7), 115 (19), 107 (22), 93 (26), 75 (57), 73 (100).

Cyclizing Grignard Reaction. 1-[2'-Methyl-1'-(trimethylsilyl)methyl-1'-propene-1'-yl]cyclopentanol (10). A flame-dried 100 mL 3-necked flask equipped with dropping funnel, Dimroth cooler and N_2 balloon was charged with Mg turnings (0.73 g, 30 mmol) in abs. THF (20 mL) and catalytic I_2. 1,4-Dibromobutane (3.24 g, 15 mmol) in 20 mL of THF was added so that the reaction started and the mixture refluxed for 20 min. Acrylic ester 9[5b] (3.21 g, 15 mmol) in THF (30 mL) was added, the mixture was refluxed overnight, cooled down and hydrolysed with saturated NH_4Cl (100 mL), ice (100 g) and methyl t-butyl ether (MTBE) (100 mL). The aqueous phase was extracted with MTBE (6 x 50 mL), the united organic phase was dried ($MgSO_4$), freed from solvent and chromatographed (Al_2O_3, activity III) giving recovered 9 (19%) and 10 (0.81 g, 24%). IR (CCl_4) 3610 m, 2950 s, 2870 s, 1620 w, 1450 w, 1250 s, 1165 m, 900 s, 852 vs, 840 s, cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.02 (s, 9 H, $SiMe_3$), 1.36 (s, 1 H, OH), 1.61 (s, 3 H, CH_3), 1.67 - 1.82 (m, 10 H, methylene), 1.87 (s, 3 H, CH_3). ^{13}C NMR ($CDCl_3$) δ 0.05 q, 20.8 t, 22.8 q, 23.7 t, 23.9 q, 40.9 t, 84.7 s, 125.1 s, 136.1 s. MS (70 eV, rt) m/z (rel. intensity) 225 (M^+-1, 0.7), 209 (M^+- OH, 6), 208 (M^+- H_2O, 35), 193 (5), 136 (7), 134 (11), 121 (13), 119 (7), 107 (10), 92 (12), 75 (9), 74 (11), 73 (100, $SiMe_3$).

1-[2'-Methyl-1'-(trimethylsilyl)methyl-1'-propene-1'-yl]cyclohexanol (11a). Ester 9 (2.0 g, 9.35 mmol), Mg (0.58 g, 24 mmol), catal. I_2, 1,5-dibromopentane (2.76 g, 12 mmol), THF (60 mL). The IR spectrum of the crude product showed a clear peak at 3600 cm^{-1} (OH), no C=O bands. Chromatography with light petroleum/MTBE (20 : 1) yielded 2.45 g of product with the following spectroscopic data. IR ($CHCl_3$) 3600 w, 3070 w, 2930 s, 2860 s, 1635 w, 1450 m, 1362 m, 1245 s, 1070 m, 1060 m, 910 m, 850 vs, cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.03 (s, 9H, $SiMe_3$), 1.18 - 1.57 (m, 8 H, 4 CH_2), 1.59 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 2.00 - 2.11 (m, 2 H, CH_2), 4.54 (m, 1 H), 4.98 (m, 2 H).

General Procedure for Cycloadditions with the (Trimethylsilyl)methyl-Terminator (cf. Table 1 and 2, Scheme 5 and 13; see also ref. 3, 5b). $TiCl_4$ (1.08 g, 5.7 mmol) under N_2 was dissolved in CH_2Cl_2 (15 mL), cooled to -20°C, mixed with N-methylaniline (0.61 g, 5.7 mmol) in CH_2Cl_2 (5 mL) and stirred for 15 min. Silylated allylic alcohol (3.8 mmol) and cyclopentadiene (0.27 g, 4.1 mmol) in CH_2Cl_2 (15 mL) were added dropwise at -25°C and the mixture was stirred for 3.5 h at -20°C, allowed to reach 0°C within 1 h and treated with pentane (20 mL) and ice-cold 1 N HCl (20 mL). The organic phase was separated and the aqueous phase was extracted with pentane (3 x 10 mL). The combined organic phase was neutralized (2 x 10 mL $NaHCO_3$ solution), washed with NaCl solution (2 x 10 mL) and dried (Na_2SO_4). After removal of the solvent the product was isolated by flash chroma-

tography (silica gel, pentane).

2,2-Diphenyl-3-methylenebicyclo[3.2.1]oct-6-ene (12). Yield 0.21 g, 21%. IR (CCl_4) 3060 m, 2950 vs, 1635 w, 1600 w, 1495 s, 1450 s, cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.75 - 1.95 [m, 2 H, C(8)H_2], 2.25 - 2.5 [m, 2 H, C(4)H_2], 2.5 - 2.67 (m, 1 H, bridgehead-H), 3.34 - 3.49 (m, 1 H, bridgehead-H, X of ABX-system), 4.61 - 4.71 (m, 1 H) and 5.07 - 5.18 (m, 1 H) (exo =CH_2), 6.05 - 6.2 (dd, 1 H) and 6.21 - 6.4 (dd, 1 H) (AB of ABX, J_{AB} = 6 Hz, J_{AX} = J_{BX} = 2.5 Hz, CH=CH), 7.15 - 7.53 (m, 10 H, 2 C_6H_5). MS (70 eV, rt) m/z (rel. intensity) 272 (M^+, 59), 231 (34), 206 (71), 205 (75), 192 (65), 191 (100), 181 (43), 178 (36), 167 (41), 165 (59), 152 (20), 141 (18), 129 (51), 115 (41), 105 (14), 91 (70), 73 (34).

2,2-Dicyclopropyl-3-methylenebicyclo[3.2.1]oct-6-ene (13). Yield 0.15 g, 20%. IR ($CHCl_3$) 3095 m, 3005 s, 2040 vs, 1630 m, 1455 m, 910 s, cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.04 - 0.4 (m, 8 H, cyclopropane CH_2), 0.66 - 1.0 (m, 2 H, cyclopropane CH), 1.58 - 2.03 [m, 2 H, C(4)H_2], 2.09 - 2.32 [m, 2 H, C(8)H_2], 2.32 - 2.6 (m, 2 H, 2 bridgehead-H), 4.78 - 4.92 (m, 1 H) and 5.0 - 5.12 (m, 1 H) (exo =CH_2), 5.86 - 6.03 (dd, 1 H) and 6.05 - 6.21 (dd, 1 H) (J_{AB} = 5.5 Hz, J_{AX} = J_{BX} = 3 Hz, CH=CH). MS (70 eV, rt) m/z (rel. intensity) 200 (M^+, 4), 185 (11), 171 (25), 159 (14), 157 (21), 142 (26), 131 (30), 129 (52), 119 (35), 117 (45), 115 (28), 105 (51), 91 (100), 79 (65). Exact mass calcd. for $C_{15}H_{20}$ m/z 200.1565; found 200.1559.

3-Methylene-bicyclo[3.2.1]oct-6-ene-2-spiro-1'-cyclopentane (14). Yield 0.15 g, 23% (0.29 g, 45% in other experiment), mint-like odour. IR (CCl_4) 3060 m, 2960 vs, 2880 s, 1635 m, 890 s, cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.42 - 2.35 (m, 12 H, 6 CH_2), 2.4 - 2.65 (m, 2 H, bridgehead-H), 4.54 - 4.72 (m, 2 H, exo =CH_2), 5.78 - 6.05 (m, 2 H, CH=CH). ^{13}C NMR ($CDCl_3$) δ 24.6 t, 24.9 t, 35.9 t, 37.2 t, 38.1 t, 39.8 d, 41.4 t, 52.4 d & s, 110.5 t, 134.4 d, 134.6 d, 153.3 s. MS (70 eV, rt) m/z (rel. intensity) 174 (M^+, 57), 159 (19), 145 (29), 133 (52), 131 (40), 117 (36), 115 (20), 109 (47), 108 (89), 105 (47), 93 (100), 91 (90), 79 (69), 77 (49), 67 (77).

3-Methylene-bicyclo[3.2.1]oct-6-ene-2-spiro-1'-cyclohexane (15). Yield 0.107 g, 15%. IR (CCl_4) 3060 w, 2940 vs, 2870 s, 1640 m, 1450 s, 910 s, cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.18 - 2.48 (m, 14 H, 7 CH_2), 2.51 - 2.61 (m, 1 H) and 2.68 - 2.88 (m, 1 H) (bridgehead-H' s); 4.6 - 4.7 (m, 1 H) and 4.74 - 4.84 (m, 1 H) (=CH_2); 5.82 - 6.06 (m, 2 H, CH=CH). MS (70 eV, rt) m/z (rel. intensity) 188 (M^+, 58), 173 (18), 159 (22), 147 (41), 131 (38), 122 (74), 105 (66), 91 (85), 79 (100), 77 (47), 67 (73). Exact mass calcd. for $C_{14}H_{20}$ m/z 188.1565; found 188.1560.

4,4-Dimethyl-3-methylene-bicyclo[3.2.1]oct-6-ene-2-spiro-1'- cyclopentane (16). 10 (0.25 g, 1.1 mmol), 2 M $TiCl_4$ in CH_2Cl_2 (0.83 mL), PhNHMe (0.18 g, 1.65 mmol), cyclopentadiene (0.20 g, 3 mmol), CH_2Cl_2 (30 mL). Yield 0.13 g, 58% after chromatography. The product may decompose on workup. IR (CCl_4) 3060 m, 2960 s, 2870 s, 1622 m, 1608 m, 1510 m, 1460 m, 1455 m, 895 m, cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.07 (s, 3 H, CH_3), 1.23 (s, 3 H, CH_3), 1.60 - 1.86 (m, 8 H, spirocyclopentane), 2.09 - 2.21 [m, 2 H, C(8)H_2], 2.39 - 2.54 (m, 2 H, bridgehead-H' s), 4.86 (s, 1H) and 4.92 (s, 1 H) (exo =CH_2), 6.04 (m, 2 H, CH=CH). MS (70 eV, rt) m/z (rel. intensity) 202 (M^+, 46), 188 (19), 187 (100, M^+- CH_3), 161 (13), 160 (13), 159 (50), 146 (27), 145 (54), 136 (52), 133 (24), 131 (27), 123 (23), 121 (27), 119 (23), 117 (23), 107 (36), 105 (37), 93 (46), 91 (47), 79 (33), 41 (29).

2,2,4,4,6-Pentamethyl-3-methylenebicyclo[5.3.0]decan-6,9-diene (21) (cf. Scheme 5 and ref. 5b, 7b). Yield of cycloadducts 1.2 g, 37%; a sample of 21 was obtained by preparative GC. ^1H NMR ($CDCl_3$, 90 MHz) δ 0.92, 1.20, 1.16, 1.24 (each

s, gem C(4)H_3, gem C(2)H_3), 1.71 (br s, 3 H, C(6)H_3), 1.73 - 1.97 (m, 1 H, H-5), 2.28 - 2.56 (m, 1 H, H-5), 2.96 (br m, 2 H, H-8), 3.34 (br m, 1 H, H-1), 4.98 (s, 2 H, exo =CH_2), 5.68 - 5.97 (m, 2 H, H-9, H-10). ^{13}C NMR ($CDCl_3$) δ 22.8, 25.1, 30.3, 30.3, 34.1, each q (5 Me), 37.7 t (C-5), 40.1 & 43.7, each s (C-2, C-4), 49.2 t (C-8), 57.1 d (C-1), 108.5 t (C-11), 127.2 s (C-6 or C-7), 130.3 & 132.9, each d (C-9, C-10), 136.8 s (C-6 or C-7), 165.6 s (C-3). MS (70 eV, rt) m/z (rel. intensity) 216 (M^+, 49), 201 (43), 173 (37), 159 (39), 145 (66), 136 (90), 131 (47), 121 (73), 111 (47), 95 (100), 91 (73). Exact mass calcd. for $C_{16}H_{24}$ m/z 216.18780; found 216.18779.

2,2,4,4-Tetramethyl-1-(1-methylethenyl)bicyclo[3.2.1]oct-6-en-3-one (26). Cycloaddition procedure in ref. 5b and below. IR (CCl_4) 2960 s, 2920 m, 1690 vs, 1630 m, 1460 m, 1370 m, 1025 m, 900 m, cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.07, 1.08, 1.18, 1.25, each s (4 x CH_3), 1.89 (br s, 3 H, olefin. CH_3), 1.89 (d, J = 12 Hz, 1 H, H-8), 2.44 (m, 1 H, H-5), 2.58 (d, J = 12 Hz, 1 H, H-8), 4.83 & 5.05 (each m, 2 H, =CH_2), 6.0 - 6.3 (m, 2 H, CH=CH). ^{13}C NMR ($CDCl_3$) δ 22.5, 23.4, 25.5, 26.2, 27.9, each q (5 Me), 39.2 t (C-8), 49.5 s (C-1), 49.7 d (C-5), 54.9 & 58.9, each s (C-2, C-4), 144.4 t (C-10), 134.9 & 138.9, each d (C-6, C-7), 145.7 s (C-9), 220.5 s (C-3). MS (70 eV, rt) m/z (rel. intensity) 218 (M^+, 55), 203 (18), 185 (6), 175 (18), 147 (82), 133 (87), 119 (66), 113 (98), 105 (76), 91 (100). Exact mass calcd. for $C_{15}H_{22}O$ m/z 218.16707; found 218.16716.

2,2,4,4,6-Pentamethylbicyclo[5.3.0]decan-6,9-dien-3-one (27). IR (CCl_4) 2980 s, 2930 s, 2860 s, 1680 vs, 1470 m, 1380 m, 1040 m, cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.89 (s, 3 H, CH_3), 1.13 (s, 3 H, CH_3), 1.20 (br s, 6 H, 2 CH_3), 1.80 (br s, 3 H, olefin. CH_3), 1.72 - 1.98 (m, 1 H, H-5), 2.48 - 2.78 (m, 1 H, H-5), 3.02 (br m, 2 H, H-8), 3.51 (br m, 1 H, H-1), 5.63 - 6.04 (m, 2 H, CH=CH). ^{13}C NMR ($CDCl_3$) δ 22.0, 22.4, 25.4, 27.5, 28.8, each q (5 CH_3), 37.4 & 45.2, each t (C-5, C-8), 49.4 & 52.8, each s (C-2, C-4), 54.4 d (C-1), 127.5 s (C-6 or C-7), 131.2 & 131.5, each d (C-9, C-10), 137.6 s (C-6 or C-7), 218.8 s (C-3). MS (70 eV, rt) m/z (Rel. intensity) 218 (M^+, 100), 203 (19), 185 (6), 175 (23), 161 (13), 153 (16), 147 (61), 133 (50), 119 (33), 113 (69), 105 (35), 91 (57). Exact mass calcd. for $C_{15}H_{22}O$ m/z 218.16707; found 218.16716.

2,2,4,4-Tetramethyl-8-(1-methylethylidene)bicyclo[3.2.1]oct-6-en-3-one (28). IR (CCl_4) 2980 m, 2930 m, 2860 m, 1700 vs, 1470 m, 1445 m, 1030 m, 905 vs, cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 6 H, 2 CH_3), 1.17 (s, 6 H, 2 CH_3), 1.77 (s, 6 H, olefin. CH_3' s), 3.04 (m, 2 H, H-1 and H-5), 6.27 (m, 2 H, CH=CH). MS (70 eV, rt) m/z (rel. intensity) 218 (M^+, 28), 203 (12), 190 (5), 175 (21), 148 (51), 133 (100), 105 (61), 91 (61).

General Procedure for Preparing Spiroannelated Ketones (33 - 35). A mixture consisting of Zn powder (9 g, 130 mmol), CuCl (1.3 g, 13 mmol) and freshly distilled cyclopentadiene (4.5 g, 69 mmol) in abs. dioxan (ca. 70 mL) was stirred vigorously at 0°C and a solution of the appropriate α,α'-dibromo ketone (46 mmol) and Me_3SiCl (6.0 g, 5 mmol) was dropped in within 2 h. The mixture was stirred for a further 10 h, being allowed to slowly reach r.t. The solid was separated by column filtration (silica gel, Et_2O) and the red brown filtrate was washed with saturated aqueous NH_4Cl, water, NaCl solution and dried ($MgSO_4$). The solvent was removed and the crude product was purified by flash-chromatography on silica gel (Et_2O/light petroleum, 1 : 10).

Instead of carrying out the reaction with mechanical stirring we have also used ultrasonic activation (30 - 50 mmol scale) for preparing 30 - 32. The preparation of 36 and 37 required ultrasonic activation.[10]

4,4-Dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one-2-spiro-1'-cyclopentane (30). 30 mmol scale, 2.23 g (38%) after double flash chromatography on silica (light petroleum/MTBE = 10 : 1). IR (CCl_4) inter al. 1700 cm^{-1} (carbonyl). ^1H NMR ($CDCl_3$, 300 MHz) δ 0.94 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 1.61 - 1.72 (m, 6 H), 2.07 (m, 1 H), 2.20 (m, 1 H), 4.42 (d, J = 1.5 Hz, 1 H), 4.47 (d, J = 1.5 Hz, 1 H), 6.34 (m, 2 H, CH=CH). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.7 q, 26.0, 26.1 & 26.2 m, 31.2 t, 38.4 t, 50.3 s, 61.5 s, 84.9 d, 86.3 d, 133.5 d, 135.2 d, 216.6 s. MS (70 eV, rt) m/z (rel. intensity) 207 (M^+ + 1, 1.7%), 206 (M^+, 15), 190 (4), 163 (5), 138 (12), 136 (71), 135 (24), 111 (10), 110 (78), 109 (22), 108 (17), 107 (47), 96 (31), 95 (100), 91 (14), 79 (24), 77 (19), 70 (37), 69 (13), 68 (26), 67 (33), 65 (15), 55 (10), 53 (19).

8-Oxabicyclo[3.2.1]oct-6-en-3-one-2-spiro-1'-cyclohexane (31). 30 mmol scale, after double flash chromatography 1.0 g, 18.5%. Best results with ultrasound; 31 decomposed on Kugelrohr distillation at 120°C, 0.1 Torr. IR (CCl_4) inter al. 1710 vs, cm^{-1} (carbonyl). ^1H NMR ($CDCl_3$, 200 MHz) δ 1.50 - 1.78 (m, 10 H), 2.08 (d, J = 1.0 Hz, 1 H), 2.36 (d, J = 1.0 Hz, 1 H), 4.81 (m, 1 H), 4.96 (dt, J = 5.0 Hz, J = 1.0 Hz, 1 H), 6.31 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 21.4, 21.6 & 25.7 m, 28.8 t, 32.0 t, 43.7 t, 56.4 s, 77.9 d, 82.5 d, 132.5 d, 134.4 d, 210.5 s. MS (70 eV, rt) m/z (rel. intensity) 193 (M^+, 3), 192 (M^+, 28), 164 (3), 149 (2), 136 (4), 125 (9), 124 (M^+ - 68, furan, 100), 111 (29), 110 (100), 109 (17), 107 (12), 93 (13), 91 (15), 83 (40), 81 (69), 79 (29), 77 (23), 68 (19), 67 (52), 55 (52), 53 (32), 44 (34), 42 (45), 40 (50).

4,4-Dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one-2-spiro-1'-cyclohexane (32). 52 mmol scale, after chromatography (pentane : MTBE = 20 : 1) 3.89 g, 42.5% of 32 are isolated. IR (CCl_4) inter al. 1700 s, cm^{-1} (carbonyl). ^1H NMR ($CDCl_3$, 200 MHz) δ 0.91 (s, 3 H), 1.32 (s, 3 H), 1.58 - 2.14 (m, 10 H), 4.41 (s, 1 H), 4.89 (s, 1 H), 6.36 (s, 2 H). ^{13}C NMR ($CDCl_3$) δ 21.1, 21.4 & 21.6 m, 25.7 t, 26.8 q, 29.7 t, 33.8 t, 51.3 s, 55.4 s, 82.0 d, 86.2 d, 113.5 d, 133.8 d, 216.8 s. MS (70 eV, rt) m/z (rel. intensity) 220 (M^+, 9), 205 (2), 152 (M^+ - furan, 11), 150 (24), 110 (70), 109 (36), 107 (29), 95 (71), 90 (27), 83 (25), 81 (52), 79 (47), 77 (35), 70 (29), 67 (29), 65 (24), 55 (43), 41 (100). Anal. calcd. for $C_{14}H_{20}O_2$ C, 76.33; H, 9.15; found C, 76.10; H 9.16.

4,4-Dimethyl-bicyclo[3.2.1]oct-6-en-3-one-2-spiro-1'-cyclopentane (33). 50 mmol scale, 5.6 g, 60%. IR (CCl_4) inter al. 1700 vs, cm^{-1} (carbonyl). ^1H NMR ($CDCl_3$) δ 1.0 (s, 3 H, eq. CH_3), 1.22 (s, 3 H, ax. CH_3), 1.46 - 2.51 (m, 12 H), 6.02 - 6.22 (m, 2 H, CH=CH). ^{13}C NMR ($CDCl_3$) δ 25.2 q, 26.1 t, 26.2 t, 28.2 q, 36.1 t, 36.2 t, 40.1 t, 49.2 d & s, 50.0 d, 61.0 s, 136.0 d, 137.2 d, 220.6 s. Exact mass calcd. for $C_{14}H_{20}O$ m/z 204.1514; found 204.1515.

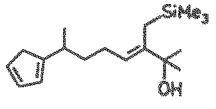
Bicyclo[3.2.1]oct-6-en-3-one-2-spiro-1'-cyclohexane (34). 46 mmol scale, 4.8 g, 55%. IR (CCl_4) inter al. 1710 vs, cm^{-1} (carbonyl). ^1H NMR ($CDCl_3$) δ 1.37 - 2.07 (m, 10 H), 2.28 (t, 2 H, CH_2), 2.42 - 2.53 (m, 2 H, CH_2CO), 2.68 - 2.94 (m, 2 H, bridgehead-H' s), 6.06 (m, 2 H, CH=CH). ^{13}C NMR ($CDCl_3$) δ 21.3 t, 21.6 t, 25.9 t, 31.6 t, 33.7 t, 37.5 t, 38.7 d, 44.1 t, 44.4 d, 54.6 s, 135.2 d, 137.0 d, 214.8 s. MS (70 eV, rt) m/z (rel. intensity) 190 (M^+, 60), 124 (100), 110 (34), 91 (32), 79 (50), 66 (29). Exact mass calcd. for $C_{13}H_{18}O$ m/z 190.1357; found 190.1358.

4,4-Dimethyl-bicyclo[3.2.1]oct-6-en-3-one-2-spiro-1'-cyclohexane (35). 50 mmol scale, 5.5 g, 55%. IR (CCl_4) inter al. 1710 vs, cm^{-1} (carbonyl). ^1H NMR ($CDCl_3$) δ 0.98 (s, 3 H, eq. CH_3), 1.16 (s, 3 H, ax. CH_3), 1.26 - 2.01 (m, 12 H),

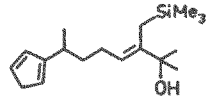
2.26 - 2.4 (m, 1 H, bridgehead-H), 2.78 - 2.96 (m, 1 H, bridgehead-H), 6.02 - 6.24 (m, 2 H, CH=CH). ^{13}C NMR ($CDCl_3$) δ 21.1 t, 21.6 t, 25.4 q, 25.8 t, 28.4 q, 32.0 t, 34.4 t, 35.2 t, 42.5 d, 49.6 d, 50.2 s, 54.5 s, 136.0 d, 136.8 d, 221.3 s. MS (70 eV, rt) m/z (rel. intensity) 218 (M^+, 71), 175 (33), 151 (21), 146 (100), 119 (26), 118 (40), 107 (50), 105 (45), 92 (76), 90 (69), 79 (38), 66 (25). Exact mass calcd. for $C_{15}H_{22}O$ m/z 218.1670; found 218.1677.

Intramolecular Cycloadditions with the Me_3SiCH_2 Terminator. (Z)-7-Methanesulfonyloxy-2-methyl-3-[(trimethylsilyl)methyl]-3-octen-2-ol (43a). 43[15] (2.4 g, 10 mmol) was dissolved in abs. pyridine (10 mL) and $MeSO_2Cl$ (1.37 g, 12 mmol) in 2 mL of abs. pyridine was added at 0°C. After addition of 4-dimethylaminopyridine (120 mg, 1 mmol) the mixture was left overnight at r.t., and worked up by carefully stirring in crushed ice and pouring the resulting mixture into ice water (50 mL). Extraction with CH_2Cl_2 (3 x 30 mL), drying ($MgSO_4$), removal of the solvent and of residual pyridine (oil pump), chromatography on silica gel (ether : light petroleum = 4 : 1) furnished 43a, 2.2 g, 68%. ^{1}H NMR (C_6H_6 standard) δ 0.03 (s, 3 H, $SiMe_3$), 1.32 (s, 6 H, 2 CH_3), 1.40 (d, J = 6 Hz, 3 H, CH_3CH), 1.54 (s, 2 H, CH_2Si), 1.5 - 2.2 (m, 4 H, CH_2CH_2), 2.9 (s, 3 H, CH_3S), 4.65 - 4.92 (m, 1 H, CHOMs), 5.26 (t, J = 7 Hz, 1 H, HC=C).

1- and 2-[6-Hydroxy-1,6-dimethyl-5-(trimethylsilyl)methyl-4-heptene-1-yl]-cyclopentadiene (44a,b).



44a



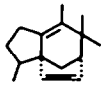
44b

Freshly distilled cyclopentadiene (0.66 g, 10 mmol) was dissolved in abs. 1,2-dimethoxyethane (4 mL) and methyllithium (5.6 mL of a 1.6 M solution, 9 mmol in Et_2O) was dropped in with precipitation of cyclopentadienyllithium. After 10 min mesylate 43a (1 g, 3 mmol) in abs. DME (5 mL) was added, the mixture being stirred at r.t. After the mesylate had disappeared (TLC control, pentane : ethyl acetate = 4 : 1) the reaction mixture was poured into 50 mL of an ice-cold solution of 10% NH_4Cl. Extraction with ether (3 x 20 mL), drying ($MgSO_4$) and chromatography (basic Al_2O_3, activity II-III, ether : light petroleum = 1 : 1) gave 44a,b, 0.75 g, 86%. The pale yellow oil was kept at -20°C, decomposing quickly at r.t. ^{1}H NMR ($CDCl_3$, Me_4Si added afterwards) δ 0.01, 0.02 (s, 9 H, $SiMe_3$), 1.15 (d, J = 6.5 Hz, 3 H, CH_3CH), 1.31 (s, 6 H, 2 CH_3), 1.58 (s, 2 H, CH_2Si), 1.51 - 2.18 (m, 4 H, CH_2CH_2), 2.45 - 2.64 (m, 1 H, CH-cp), 2.89 (d, J = 1.5 Hz, 2 H, CH_2 in cp 44a), 2.98 (b s, 2 H, CH_2 in 44b), 5.27 (t, J = 7 Hz, 1 H, HC=C), 6.01, 6.18, 6.30, 6.46 (m, 3 H, CH in cp 44a,b). MS (70 eV, rt) m/z (rel. intensity) 292 (M^+, 2), 277 (2), 276 (2), 274 (2), 233 (5), 202 (13), 187 (19), 159 (29), 145 (18), 133 (52), 132 (30), 131 (20), 119 (30), 117 (27), 93 (48), 91 (38), 75 (41), 73 (100).

2,2,7-Trimethyl-6-methylene-tricyclo[6.2.1.$0^{1,5}$]undec-9,10- ene (45) (9,10-Dehydrozizaene). a) Fixed bed catalyst. Anhydrous $ZnCl_2$ (6, 44 mmol) was dissolved in abs. ether (300 mL) and 200 g of neutral Al_2O_3, activity I was added. The ether was evaporated and the catalyst was stored under N_2 in a well-stoppered vessel. 100 g of catalyst contained 3% $ZnCl_2$ (22 mmol). b) Intramolecular Cyclization. Trifluoroacetic anhydride (0.63 g, 0.42 mL, 3 mmol) in abs. CH_2Cl_2 (5 mL) was cooled to -70°C and $EtNPr^i_2$ (0.41 g, 0.54 mL, 3.2 mmol) in CH_2Cl_2 (5 mL) was slow-

ly added. At -70°C and under N_2 allylic alcohol **44a,b** (0.7 g, 2.4 mmol) in abs. CH_2Cl_2 (15 mL) was dropped in. The mixture was stirred for 3 h at -70°C, diluted with precooled pentane (150 mL) and the resulting crude trifluoroacetate was passed dropwise through a column which was made up from 160 g of activated Al_2O_3 (36 mmol of $ZnCl_2$, 15 eq) in pentane and cooled externally to -60°C. The column was eluted with pentane (150 mL) and the combined eluate was collected in a flask containing K_2CO_3 and equipped with a $CaCl_2$ tube. The pentane was evaporated down to 50 mL and filtered through a short column of silica gel to destroy unreacted trifluoroacetate. The column was washed with a little pentane, the solvent was evaporated and the residue was distilled (Kugelrohr, 80°C/1 Torr), giving 78 mg, 16% of isomeric 9,10-dehydrozizaenes (**45**). ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.90 (d, J = 6 Hz, 3 H, CH_3 at C-2), 0.94 (d, J = 5 Hz, 3 H, CH_3 at C-2), 1.05, 1.13, 1.19 (s, 6 H, CH_3 at C-7), 1.40 - 1.95 (m, CH_2), 1.95 - 2.25 (m, CH), 4.61, 4.79, 4.85, 4.95 (m, CH_2=C), [5.53 s, 5.60 (d, J = 1 Hz), 5.69 (d, J = 1.5 Hz), 5.76 s, 5.99 m] (HC=CH).

NB. In naturally occuring zizaene the C-2 methyl group appears at 0.94 ppm, J = 6.5 Hz according to Yoshikoshi.[16] Two signals (1.05, 1.19 ppm) of the three observed signals for the geminal CH_3 protons in **45** are somewhat broadened. The olefinic signals are very similar to those of 9,10-dehydro-2-norzizaene. In analogy to Henning's interpretation[3] the exo-methylene signals at 4.61 and 4.85 ppm are assumed to be due to the two trans-fused isomers **45a** and **45b** and the signals at 4.79 and 4.95 ppm to the cis-isomers **45c** and **45d**. The combined GC-MS and NMR data prove structure **45**. The hydrogenation of the endocyclic double bond in **45**, which was accomplished for 9,10-dehydro-2-norzizaene with diimide in 95% yield,[3] was not carried out, since the dehydro derivative was more interesting, both mechanistically and synthetically. Apart from the three major $C_{15}H_{22}$ product peaks, GC-MS revealed a further small peak (at higher retention time) of mass 202 (4% of **45**), which showed a fragmentation pattern very similar to **45**. The formation of endocyclic isomer **i** is a possibility.



i

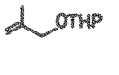
GC-MS (according to increasing retention time) isomer **A**: m/z = 202 (M^+, 15), 187 (30), 173 (4), 159 (42), 145 (35), 132 (42), 117 (52), 106 (25), 91 (100), 77 (27), 67 (12). Isomer **B**: m/z = 202 (M^+, 25), 187 (42), 173 (3), 159 (50), 145 (30), 132 (50), 117 (55), 105 (30), 91 (100), 77 (30), 67 (12). Isomer **C**: m/z = 202 (M^+, 25), 187 (25), 173 (2), 159 (57), 145 (30), 131 (37), 117 (62), 105 (32), 91 (100), 77 (35), 67 (15). Product **i**: m/z = 202 (M^+, 37), 187 (42), 174 (7), 159 (67), 145 (35), 132 (82), 117 (80), 105 (40), 91 (100), 77 (42), 67 (17). Exact mass calcd. for $C_{15}H_{22}$ m/z 202.1722; found 202.1722.

NB. The three major products **A**, **B** and **C** were formed in a ratio of 1 : 1.06 : 2.86. Since all four isomers **45a-d** should have been formed in about equal ratio, it is assumed that two isomers had the same retention time. The ratio of the sum of the two smaller peaks to the bigger peak was 1 : 1.39. In earlier work cis/trans-9,10-dehydro-2-norzizaene was formed in a ratio of 1 : 1.15.[3] The trans isomer had the longer retention time. Therefore, the two trans isomers **45a** and **45b** probably had the same retention time, whereas the cis isomers **45c** and **45d** were separated.

7,7-Dimethyl-2,6-dimethylenetricyclo[6.2.1.$0^{1,5}$]undec-9,10-ene (47). A solution of $TiCl_4$ (0.17 mL, 1.5 mmol) in abs. CH_2Cl_2 (10 mL) was kept under N_2 and N-methylaniline (0.16 g, 1.5 mmol) in 2 mL of CH_2Cl_2 was slowly dropped in at -20° to -30°C. The resulting deep-red mixture was stirred for 15 min at -20°C. Now vinylcyclopentadienes 46[7] [the 1- and 2-substituted isomers (2 : 1)] (ca. 1.4 mmol) in 10 mL of abs. CH_2Cl_2 were added at -20°C. the mixture was stirred for 2 h, poured into ether (100 mL), washed with water (3 x 50 mL) and dried ($MgSO_4$). After removal of the solvent the remaining oil was taken up in pentane and filtered through a short column of silica gel. The pentane was evaporated to leave an oil which was distilled (Kugelrohr, bp 80-90°C/1 Torr), giving a pale yellow liquid; 35 mg, ca 20% w.r.t. 1-substituted isomer of 46. ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.09, 1.23 [each br s, 6 H, 7 -$(CH_3)_2$], 1.50 - 1.95 (m, 4 H, 4-H_2, 11-H_2), 2.0 - 2.75 (m, 4 H, 3-H_2, 5-H, 8-H), 4.55 - 5.05 (m, 4 H, 2x =CH_2), 5.45 - 6.15 (m, 2 H, CH=CH). MS (70 eV, rt) m/z (rel. intensity) 200 (M^+, 50), 185 (100), 157 (50), 143 (23), 131 (53), 130 (67), 117 (23), 115 (24), 105 (12), 91 (50), 79 (19), 77 (23), 67 (13), 65 (16), 53 (16), 41 (30).

NB. The molecular ion shows a high relative intensity of 50%.

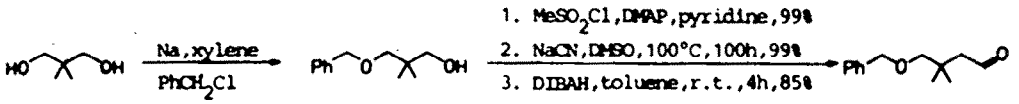
Preparation of Allylic Alcohols 40 and 49 with 2-Tetrahydropyranyloxy Terminator. a) 2-Methyl-1-(2-tetrahydropyranyloxy)-1-propene (48). 2-Methyl-3-(2-tetrahydropyranyloxy)-1-propene (ii) (80 g, 0.512 mol) was stirred with $KOBu^t$ (4 g, 33 mmol) under N_2 for 4 h at 170° - 180°C. Direct distillation, bp 80°C/17 Torr gave 48 (61.6 g, 77%). IR (CCl_4) 2940 s, 1690 m, 1160 vs, 1035 vs, cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.13 - 2.06 (m, 6 H, 3 CH_2), 1.59 (d, J = 1.4 Hz, 3 H), 1.67 (d, J = 1.4 Hz, 3 H), 3.33 - 4.11 (m, 2 H, OCH_2), 4.84 (m, 1 H, CH), 6.01 (t, J = 1.4 Hz, 1 H, =CH). MS (70 eV, rt) m/z (rel. intensity) 156 (M^+, 17), 86 (12), 85 (100), 79 (9), 67 (18), 57 (27), 55 (13). b) Lithiation and Quenching with Carbonyl Compound. General Procedure. THP-Vinyl ether 48 (21.8 g, 0.14 mol) was dissolved in abs. THF (250 mL) and cooled to -78°C (MeOH, solid CO_2). Then 0.14 mol of a solution of s-butyllithium in hexane (concentration 0.6 - 1.3 mol/L) was added slowly with stirring. The mixture was kept at -70°C overnight and Et_2O (80 mL) was added slowly. The mixture was cooled to -120°C (n-propanol/liq. N_2) and aldehyde (or ketone) (0.12 mol) in Et_2O (40 mL) was dropped in very slowly through a dropping funnel cooled externally with MeOH/solid CO_2. After completed addition the cooling bath was removed. When the reaction mixture had reached -30°C it was poured onto water (100 mL). The aqueous phase was extracted with Et_2O (3 x 50 mL) and the organic phase was washed with aqueous NaCl solution (2 x 100 mL) and dried (Na_2SO_4). The solvent was taken off on a rotary evaporator, the residue was stirred at r.t./0.1 Torr for 1 h and chromatographed on silica gel (Et_2O/light petroleum, 1 : 9 and then 1 : 1). Unreacted aldehyde/ketone and THP-vinyl ether were recovered from the first fractions.



ii

2,4-Dimethyl-3-(2-tetrahydropyranyloxy)-3-penten-2-ol (40). Colourless oil, bp 90°-100°C/0.1 Torr, 11.9 g (40% yield). IR (CCl_4) 3460 br m, 3000 vs, 2970 vs, 2940 vs, 2860 s, 1657 w, 1380 vs, 1130 vs, 1070 vs, 1030 vs, cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.1 - 2.2 (m, 6 H, $CH_2CH_2CH_2$), 1.44 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.68 (s, 3 H, olefin. CH_3), 1.78 (s, 3 H, olefin. CH_3), 3.3 - 3.67 (m, 1 H), 3.83 - 4.18 (m, 1 H), 3.95 (s, 1 H, OH), 4.31 - 4.56 (m, 1 H). ^{13}C NMR ($CDCl_3$) δ 19.6 q, 20.3 q, 21.7 t, 25.0 t, 29.5 q, 30.0 q, 31.2 t, 65.6 t, 71.5 s, 104.2 d, 116.8 s, 154.7 s.

4-(t-Butyldimethylsilyloxy)-5-(2-tetrahydropyranyloxy)-2,2,6-trimethyl-5-hepten-1-ol (50). 4-Benzyloxy-3,3-dimethyl-1-butanal (111) was prepared in three simple steps (Scheme 16) and converted into 49 via lithiation of 48 (cf. also



111

48 → 50). 15.5 g (75 mmol) of 111 gave 49 (16.7 g, 61%), colourless oil, as a diastereomeric mixture which was converted directly into TBDMS-ether (93%) and debenzylated (Li, THF/liq. NH_3, 1 : 1) giving 50 (11.2 g, 81%), colourless oil. ^1H NMR ($CDCl_3$) δ 0.03 (s, 3 H, SiMe), 0.09 (s, 3 H, SiMe), 0.88 (s, 9 H, CMe_3), 0.76 - 1.0 [m, 6 H, $-C(CH_3)_2-$], 1.1 - 2.2 (m, 14 H), 2.7 - 3.37 (m, 3 H, CH_2OH), 3.2 - 4.15 (m, 2 H, $-OCH_2CH_2$), 4.65 (m, 1 H, CHOSi), 4.9 - 5.3 (m, 1 H, OCHO).

7-(1,3-Cyclopentadienyl)-4-(t-butyldimethylsilyloxy)-3-(2-tetrahydropyranyloxy)-2,6,6-trimethyl-2-heptene (52). Oxidation of 50 (9.2 g) with PDC in CH_2Cl_2 (70 mL) gave, after 48 h at r.t., the aldehyde (2.66 g, 64% after chromatography on silica gel), which was converted (NaH, THF, cyclopentadiene, 30 min, r.t.) into fulvene 51 (48%) (cf. ref. 7), bright yellow oil. Reduction with $LiAlH_4$ in THF (15 min, r.t.) gave 52 (1.02 g, 92%), colourless oil, diastereomeric mixture. ^1H NMR ($CDCl_3$) δ 0.02 (s, 3 H, SiMe), 0.08 (s, 3 H, SiMe), 0.87 [s, 15 H, CMe_3, $C(CH_3)_2C$], 1.1 - 2.05 (m, 14 H), 2.19 - 2.38 (m, 2 H, CH_2 cp), 2.94 (br s, 2 H, CH_2 in cp), 3.27 - 3.64, 3.86 - 4.19 (m x 2, 2 H, OCH_2), 4.53 - 4.86 (m, 1 H, CHOSi), 4.93 - 5.10 (m, 1 H), 5.93 - 6.53 (m, 3 H, =CH- in cp). The product should be used immediately for the next step.

Cycloadditions with the OTHP-Terminator. 2,2,4,4-Tetramethylbicyclo[3.2.1]-oct-6-en-3-one (41). Two equivalents of $TiCl_4$/PhNHMe[6] were used in these reactions. N-methylaniline (0.73 g, 6.8 mmol) in CH_2Cl_2 (3 mL) was stirred dropwise into 3.4 mL (6.8 mmol) of a 2 M $TiCl_4$ solution in abs. CH_2Cl_2 under N_2 at 0°C. The mixture was stirred for 15 min, cooled to -15° to -20°C and a mixture of 3.4 mmol of alcohol 40 (0.73 g) and cyclopentadiene (0.7 g, 10.6 mmol) in CH_2Cl_2 (10 mL) was stirred in slowly at -20°C. After 1 h the cooling bath was removed and the reaction temperature was allowed to reach 0°C. After addition of ether (30 mL) and 1 N HCl (30 mL) the aqueous phase was separated and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phase was washed with aqueous $NaHCO_3$ (2 x 30 mL), aqueous NaCl (20 mL) and dried (Na_2SO_4). After removal of the solvent the crude product was flash-chromatographed on silica gel (CH_2Cl_2) giving 41[5b] (0.26 g, 44%).

3,3,7,7-Tetramethyl-tricyclo[6.2.1.$0^{1,5}$]undec-9,10-en-6-one (53). 52 (1.0 g, 2.3 mmol) in CH_2Cl_2 (25 mL) was dropped slowly into a freshly prepared solution of $TiCl_4$ (0.87 g, 4.6 mmol) and PhNHMe (0.49 g, 4.6 mmol) in CH_2Cl_2 (25 mL) at -15° to -20°C. After complete addition the mixture was stirred for another 45 min, allowed to reach 0°C and worked up as above. Chromatography (silica gel, ether/light petroleum, 3 : 7) gave 245 mg (54% w.r.t. 52) product containing 55% of 53. A second chromatography gave 42.0 mg (17%) mainly containing isomer 53a and 26.7 mg (11%) mainly containing isomer 53b (53b : 53a = 39 : 61). trans-Hydrindane isomer 53b: IR ($CHCl_3$) 3060 s, 2960 s, 2940 s, 2880 m, 1705 vs (C=O), 1600 bw, 1463 m, 1388 m, 1370 m, 1090 w, 1075 w, cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz) δ 1.02 (s, 3 H, eq. CH_3 at C-7), 1.09 [s, 3 H, CH_3-C(3)], 1.15 [s, 3 H, CH_3-C(3)], 1.24 (s, 3 H,

ax. CH_3 at C-7), 1.3 - 2.2 (m, 6 H), 2.33 - 2.51 (m, 1 H, H-8), 2.93 (X of ABX, 1 H, H-5), 5.87 (A of ABX, $J_{H-9,H-10}$ = 6.0 Hz, H-10), 6.11 (B of ABX, $J_{H-9,H-10}$ = 6.0 Hz, $J_{H-8,H-9}$ = 3.0 Hz, 1 H, H-9). MS (70 eV, rt) m/z (rel. intensity) 218 (M^+, 76), 203 (15), 175 (32), 148 (57), 147 (100), 133 (21), 121 (21), 119 (27), 105 (42), 92 (46), 91 (50), 79 (17). Exact mass calcd. for $C_{15}H_{22}O$ m/z 218.16707; found 218.16736.

cis-Hydrindane isomer **53a**: IR ($CHCl_3$) 3060 w, 2963 s, 2940 s, 2878 m, 1696 vs (C=O), 1600 bw, 1465 m, 1382 w, 1370 w, 1362 w, 1350 w, 1120 w, 910 w, 838 w, cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz) δ 1.00 (s, 3 H, eq. CH_3 at C-7), 1.02 (s, 3 H, CH_3 at C-3), 1.09 (s, 3 H, CH_3 at C-3), 1.18 (s, 3 H, ax. CH_3 at C-7), 1.3 - 2.2 (m, 6 H), 2.33 - 2.51 (m, 1 H, H-8), 2.60 (d, J = 2.0 Hz, 1 H, H-5), 6.02 (m, 2 H, H-9, H-10). MS (70 eV, rt) m/z (rel. intensity) 218 (M^+, 56), 203 (10), 175 (26), 148 (48), 147 (100), 133 (19), 119 (22), 105 (38), 92 (38), 91 (50), 79 (15), 77 (18). Exact mass calcd. for $C_{15}H_{22}O$ m/z 218.16707; found 218.16736.

Equilibration. Na (0.065 g, 2.8 mmol) was dissolved in methanol (5 mL) and **53b** (35 mg) was added. After being stirred for 24 h under N_2 the mixture was worked up by addition of water (30 mL), extraction with pentane (4 x 20 mL), washing with aqueous NaCl (2 x 30 mL) and drying (Na_2SO_4). Yield 29.7 mg (85%), **53b** : **53a** = 54 : 46. The ^1H NMR spectrum showed no decomposition products.

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