237. Silicon-Directed *Nazarov* Reactions III. Stereochemical and Mechanistic Considerations

by **Todd K. Jones** and **Scott E. Denmark***

Roger Adams Laboratory, School of Chemical Sciences University of Illinois, Urbana, IL 61801

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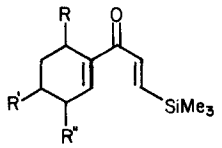
Summary

The influence of remote substituents on the stereochemical outcome of electrocyclization in the silicon-directed *Nazarov* reaction has been examined. While the degree of stereocontrol was modest (*ca.* 3:1) the substituent in the major isomer (4,5 or 7-substituted *cis*-hexahydroind-2-en-1-ones) is always *cis* to the protons on the ring fusion. Thorough spectroscopic and conformational analysis revealed that divergent senses of electrocyclization are responsible for the observed products. Additional experiments suggest that steric, rather than stereoelectronic forces control the sense of cyclization. A qualitative description of the nature of reactive intermediates in the silicon-directed *Nazarov* reaction is proposed as well as an explanation for the remarkable efficacy of $FeCl_3$ for inducing the reaction.

Introduction. – In the preceding paper a general procedure for the synthesis of 4,5-disubstituted and 4,5-annelated-2-cyclopentenones with complete control over regiochemistry of the double bond was described. The utility of this reaction in the synthesis of complex cyclopentanoid natural products would be enhanced if the creation of the two new chiral centers associated with cyclization process could be directed by remote chiral centers already present in the substrate. Since the *Nazarov* cyclization (and presumably this variant) is an electrocyclic reaction [1] and therefore subject to orbital symmetry control [2] the molecular motions and intermediates involved in creating the new chiral centers should be well defined. This paper describes the results of an investigation to determine *1*) the influence of remote substituents on the ring-forming process, *2*) the nature of the intermediates involved and *3*) the reasons for the unique ability of $FeCl_3$ to induce the cyclization.

Stereocontrol. – 1. *Results.* – Our selection of substrates for the examination of stereochemical control was guided by the high degree of relative control of stereochemistry (100% *cis*) at the ring fusion in hexahydro-2-inden-1-one. Incorporation of substituents into the six-membered ring was simple, and we have examined the three divinyl ketones **1**–**3**. In each case the substrate reacted smoothly under standard condi-



R = CH_3, R', R'' = H: **1**
R' = *t*-Bu, R, R'' = H: **2**
R'' = CH_3, R, R' = H: **3**

tions (> 80% yields) to afford a mixture of two stereoisomeric products[1]). The assignment of stereochemistry of all products was done by a combination of spectroscopic and conformational analysis of the mixtures which could be resolved only by capillary GC or HPLC. The *Table* summarizes all of the pertinent chemical shift and coupling constant data which aided in assignment of stereochemistry. Fortunately, the isomers were formed in unequal amounts which permitted ready assignment of individual resonances. The coupling constants in the six-membered were all obtained by double resonance experiments at 360 MHz, while the others ($J(2,3a)$ and $J(3,3a)$) could be determined by inspection. To simplify description of the isomers involved and to relate families of isomers we use a nomenclature which employs two descriptors, each can be either *cis* (*C*) or *trans* (*T*). The first descriptor in a pair defines the ring-fusion stereochemistry and the second defines the relationship between the H-atom at the remote chiral center and the *H-atom at C(3a)*. Each case will be discussed separately.

Table. *^1H Chemical Shifts and ^1H, ^1H-Coupling Constants for Cyclization Products*

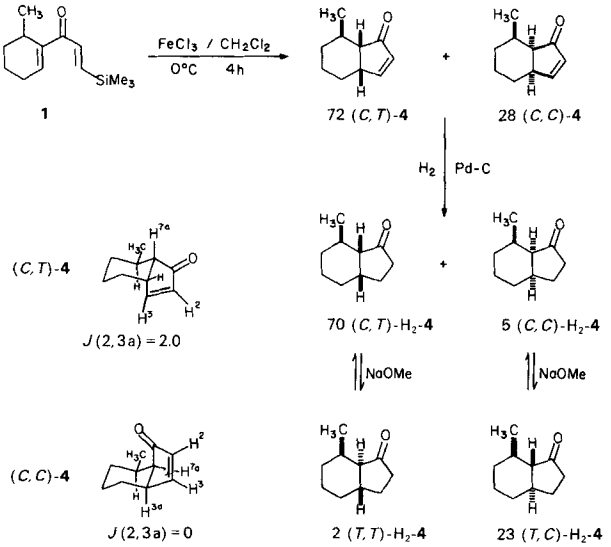
Compound	Substituents	H–C(2)	H–C(3)	H–C(3a)	H–C(7a)
(*C*,*T*)-**4**	$R^1 = CH_3$, R^2–R^6 = H	6.13	7.54	2.96	2.02
(*C*,*C*)-**4**	$R^1 = CH_3$, R^1, R^3–R^6 = H	6.10	7.54	3.09	2.41
(*C*,*T*)-**5**	R^3 = *t*-Bu, R^1, R^2, R^4–R^6 = H	6.18	7.69	3.20	2.34
(*C*,*C*)-**5**	R^4 = *t*-Bu, R^1–R^3, R^5, R^6 = H	6.11	7.55	2.92	2.30
(*C*,*T*)-**6**	$R^5 = CH_3$, R^1–R^4, R^6 = H	6.16	7.84	2.48	2.39
(*C*,*C*)-**6**	$R^6 = CH_3$, R^1–R^5 = H	6.26	7.72	3.03	2.48
7	R^1–R^6 = H	6.14	7.64	2.96	2.4

Compound	Substituents	$J(2,3a)$	$J(3,3a)$	$J(4,3a)$	$J(3a,7a)$	$J(7\alpha,7a)$	$J(7\beta,7a)$
(*C*,*T*)-**4**	$R^1 = CH_3$, R^2–R^6 = H	2.0	2.5	–	2.8	8.7	–
(*C*,*C*)-**4**	$R^1 = CH_3$, R^1, R^3–R^6 = H	0	2.5	–	6	–	5.5
(*C*,*T*)-**5**	R^3 = *t*-Bu, R^1, R^2, R^4–R^6 = H	1	2.8	–	6	6	6
(*C*,*C*)-**5**	R^4 = *t*-Bu, R^1–R^3, R^5, R^6 = H	1	2.2	–	6	6	6
(*C*,*T*)-**6**	$R^5 = CH_3$, R^1–R^4, R^6 = H	1	2.9	–	6	–	–
(*C*,*C*)-**6**	$R^6 = CH_3$, R^1–R^5 = H	2.9	2.9	6	6	–	–
7	R^1–R^6 = H	1.1	2.8	–	6.2	–	–

[1]) The stereoisomeric nature of the components was supported by a correct elemental analysis for the mixture.

1.1. Cyclization of **1.** *Scheme 1* summarizes the results of cyclization of **1** with a CH_3-group in the 6'-position. The rate of reaction and yield are nearly identical to that observed in the unsubstituted case. HPLC analysis of the product mixture revealed the presence of two stereoisomeric components in a 28:72 ratio (elution order). While we assumed that both isomers had a *cis*-ring fusion based on previous experience, the complete stereochemical description was achieved as follows. The vicinal coupling constants $J(3a,7a)$ for both the major (2.8 Hz) and minor (6.0 Hz) isomers was in the range for a *cis* ring fusion [3]. Further $J(7,7a)$ for the major isomer (8.7 Hz) is larger than that for the minor isomer (5.5 Hz) suggesting a larger dihedral angle and thus a *trans*-relationship. This evidence, while consistent, is by no means conclusive, so we made use of additional, chemical information which was easily obtained.

Scheme 1



Catalytic hydrogenation of the mixture produced (96% yield) a new 28:72 mixture (elution order from capillary GC) of saturated ketones. Removal of the double bond locks the two isomers into their configurational families, *i.e.* the relationship between H–C(3a) and H–C(7) cannot change. If the two isomers differ only in ring-fusion stereochemistry, then epimerization at C(7a) should only change the relative amounts of the two components. If, however, the two isomers differ only in the stereochemistry at the remote center, then epimerization can produce two new isomers at the expense of the original ones, but pairwise sums of each original component and its daughter must reproduce the starting ratio[2]). In this case, conformational analysis of the pairs of C(7a)-epimers allows a prediction of the major contributor at equilibrium for each family of isomers.

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[2]) This latter situation will also be obtained in the unlikely event that the isomers differ in both stereochemical senses. In this case, again, the ratio of a component and its daughter allows assignment.

In the event, base-catalyzed epimerization (1 mol-% $NaOCH_3/CH_3OH$, 20°) resulted in the formation of *two new* isomers[3]) the parentage of which was easily determined by pairwise summation (see *Scheme 1*). Thus, the major dihydro isomer gives rise to a new component which comprises only 3% of their equilibrium (2:70), while the minor dihydro-isomer gives rise to a fourth component which in fact dominates their equilibrium by a factor of 4.6 (23:5). It is therefore clear that the original isomers belonged to different families. This information was used to test the assignment based on interproton coupling. Assuming the original major isomer is (*C*,*T*)-**4**, then the conformation shown in *Scheme 1* should be preferred since the CH_3-group assumes an equatorial orientation. It can now be appreciated that the dihydro derivative ((*C*,*T*)-H_2-**4**) cannot readily epimerize at C(7a) since that would lead to an impossibly strained, *trans*-diaxially fused system. Epimerization can occur however, after a ring inversion which places the CH_3- and carbonyl groups in axial orientations. Epimerization at C(7a) now leads to (*T*,*T*)-H_2-**4** with a diequatorially fused system. The requirement of forcing the CH_3-group axial is consistent with the minimal contribution of this isomer to a (*C*,*T*)⇌(*T*,*T*) equilibrium. Similarly, if the original minor isomer is (*C*,*C*)-**4**, then the conformation shown in *Scheme 2* should be preferred due to the orientation of the methyl group. Epimerization at C(7a) should be facile and indeed we observed that the new component predominated at equilibrium. This is fully consistent with the observation of *House & Rasmussen* [4] that (*T*,*C*)-H_2-**4** is favored at equilibrium with (*C*,*C*)-H_2-**4** by a factor of 3.1[4]). It is thus established that the products of silicon-directed cyclization both have a *cis* ring fusion and that in the major isomer (*C*,*T*) the cyclopentenone ring and the substituent are *trans*-disposed.

1.2. Cyclization of **2**. *Scheme 2* summarizes the results of an analogous series of experiments with **2**. Placement of a *tert*-butyl group in the 4'-position had no great effect on the rate (4 h/0°) yield (82%) or selectivity of the reaction. HPLC analysis of the product revealed a 25:75 (elution order) mixture of isomers[1]). Determination of the coupling constants between the relevant protons in these isomers led to a surprising conclusion. From the data on the *Table* it can be seen that *J*(3a,7a) for both of the isomers is consistent with a *cis* ring fusion (6 Hz). Remarkably, the coupling constants *J*(7α,7a) and *J*(7β,7a) are the same for both isomers. While this is consistent with the conformation shown for (*C*,*C*)-**5** (H–C(7a) bisects H–C(7α) and H–C(7β)), it is inconsistent with the chair conformation proposed for (*C*,*T*)-**5**. We suggest that the boat conformation shown in *Scheme 3* better fits this data as well as the trend in allylic coupling constants which will be discussed later.

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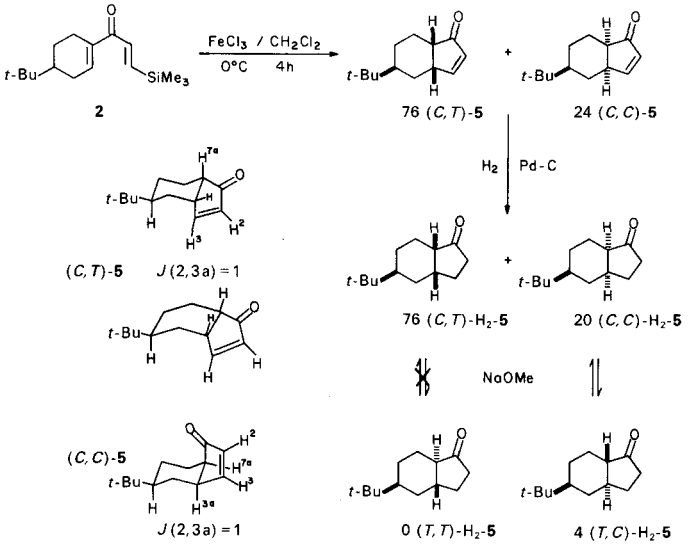
[3]) The stereoisomeric nature of the three major components in this mixture (97.7%) was assured by capillary GC-MS measurement which showed a strong molecular ion (*m*/*z* = 152) and characteristic fragmentation pattern. The minor component (t_R 6.85, (*T*,*T*)-H_2-**4**) gave too few ions for an MS.

[4]) Several explanations for the difference in equilibrium ratios can be entertained: 1) the HPLC and GC are not calibrated for different response factors, but the ratio does not change between UV detection (LC) and flame-ionization detection (GC); 2) the methods of integration differ, we employ an *HP-3390* electronic integrator accurate to 1% and 3) the conditions of equilibration differ, *House* [4] used Et_3N/100°, compared to our $NaOCH_3/CH_3OH$/20°.

Schema 2



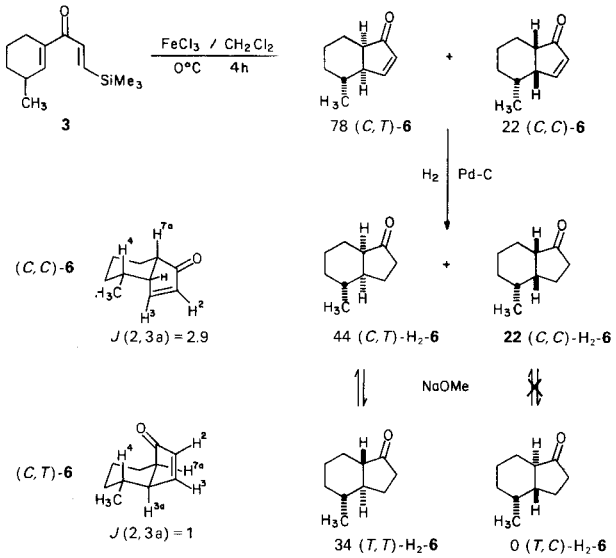
Catalytic hydrogenation of the mixture produced a new 25:75 mixture of perhydroindenones[5]) (capillary GC analysis). MeONa-catalyzed epimerization produced only one new component at the expense of the minor dihydro isomer. The reluctance of the original major isomer to epimerize is consistent with its assignment of (*C*, *T*)-H_2-**5** stereochemistry for the reasons described for (*C*, *T*)-H_2-**4** *(vide supra)*. In this case a *tert*-butyl group would have to become axial (or pseudoaxial) in the (*T*, *T*)-H_2-**5** form. The position of the equilibrium for C(7a) epimers of the minor dihydro isomer (5:1) is consistent with assignment of the original minor isomer as (*C*, *C*)-**5**. We suspected that the 5-*tert*-butyl group would not seriously perturb the equilibrium distribution normally observed for 1-indanone which has been determined [4] to favor the *cis*-isomer by a factor of 3; (*C*, *C*)-H_2-**5** is favored over (*T*, *C*)-H_2-**5** by a factor of 5. Thus, the outcome of the cyclization is analogous to that observed from **1** *i.e.*: both isomers possess a *cis* ring fusion and in the major isomer the five-membered ring and the substituent are *trans*.

1.3. Cyclization of **3**. The results of cyclization of **3** and stereochemical analysis of the products are summarized in *Scheme 3*. An excellent yield (99%) of a 78:22 mixture of stereoisomers[1]) was obtained. A firm stereochemical assignment from ^{1}H-NMR spectroscopy was hampered by the coincidence of H–C(3a) in the major and H–C(7a) in the minor isomers *(Table)*. Identical *J*(3a, 7a)-values in each isomer suggested a *cis* ring fusion in both. Hydrogenation (87%) and MeONa equilibration resulted in ternary mixture of dihydro isomers[6]) in which the new component was formed

[5]) The identity of these compounds was assured by independent synthesis of **8** *(vide infra)* and GC coinjection.

[6]) The assignment of all three components as stereoisomers was supported by capillary GC-MS measurement which showed strong molecular ions (m/z = 152) for each peak as well as a characteristic fragmentation pattern.

Scheme 3

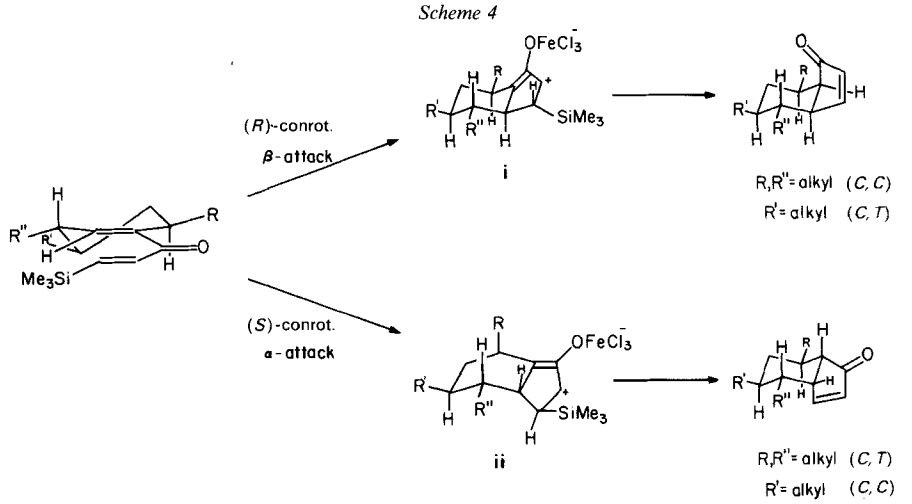


solely at the expense of the original major isomer. The assignment of that isomer as (*C*, *T*)-**6** follows from consideration of its most stable conformation shown in *Scheme 3*. Epimerization at C(7a) of its dihydro derivative should be facile (axial carbonyl group) and, in fact, an equilibrium was established ($k_{eq} = 1.3$) favoring (*C*, *T*)-H_2-**6**. That the minor product from cyclization is the (*C*, *C*)-**6** isomer is supported by the absence of a C(7a) epimer from equilibration of its dihydro derivative. This would require an axial C(4)-methyl group. In summary, all three substrates examined produced roughly 3:1 mixtures of *cis*-fused products wherein the major component was always the (*C*, *T*)-isomer.

Before discussing the implication of these results and other experiments, several trends in the isomers of **4**, **5** and **6** are noteworthy. First, regarding polarity and volatility it appears that the *cis*-isomer which has an axial carbonyl group is less polar and more volatile. This is true for both enones and saturated ketones. Second, inspection of the allylic coupling constant $J(2,3a)$, for all six isomers *(Table)* reveals that this may be used as a reliable index of conformation in *cis*-hexahydro-2-inden-1-ones. Theory predicts [5] that the coupling constant should be at a maximum ($|J| = 3$ Hz) when the allylic proton is normal (90°) to the olefin plane and minimal ($J = 0$) when the proton is contained in the plane. Examination of molecular models of **4**–**6** shows that the former condition is met when the allylic proton H–C(3a) is equatorial and the latter when it is axial to the six-membered ring (see *Schemes 1–3*). This further supports the suggestion that (*C*, *T*)-**5** exists in a boat conformation since a chair would be expected to have $J(2,3a) = 2$ Hz. Finally, this trend allows evaluation of the preferred conformation of the unsubstituted hexahydro-2-inden-1-one **7**. The magnitude of $J(2,3a)$ (1.1 Hz) suggests that the conformation which holds the carbonyl in an axial orientation is preferred.

2. Discussion. – While the degree of remote stereocontrol in **4–6** was modest, it was actually surprising that (*C*, *T*)-isomers always predominated. Consideration of the molecular motions involved reveals that *two different modes of electrocyclization* are in fact responsible for the major isomers. The two conrotatory senses of electrocyclization and their stereochemical consequences are diagrammed in *Scheme 4*. They are defined as

Scheme 4

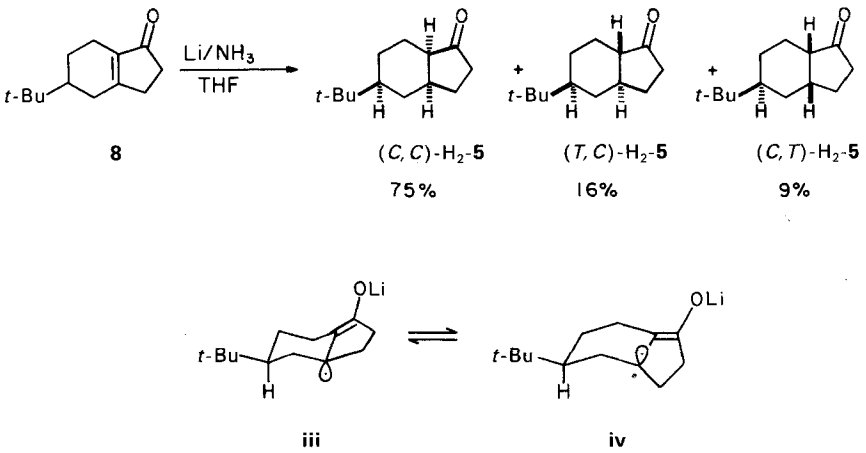


clockwise (*R*) or counterclockwise (*S*) conrotations taking as reference point the view from behind the divinyl ketone. The substituents (R, R′, R″) are assumed to take up equatorial (C(4′)) or pseudoequatorial (C(3′), C(6′)) positions in the cyclohexane half-chair. The Me_3Si group and H–C(2′) serve as markers to visualize the motions. A necessary consequence of (*R*)-conrotation is attack on the β-face of the internal double bond giving rise to intermediate ***i*** in which the new C–C-bond and any of the substituents are equatorial in the chair conformation. This step establishes to which stereochemical family the product will belong since subsequent steps (loss of Me_3Si^+ and protonation) must lead to *cis*-fused isomers only. Thus, intermediate ***i*** leads to the *minor* isomers (*C*, *C*) from **1** and **2** and the *major* isomer (*C*, *T*) from **3**.

In the (*S*)-conrotation mode, attack at the α-face of the internal double bond is intimately coupled to the cyclization process. However, the *new C–C-bond formed in* ***ii*** *cannot be axially disposed* because the C(1)–C(7a) double bond requires that C(1), C(2), C(3a) and C(7a) be coplanar. Thus, ***ii*** must choose between a skew boat conformation or a chair conformation in which the substituent will be axial. It should be emphasized that the inability of the new C–C-bond to assume an axial orientation necessarily removes any stereoelectronic preferences normally associated with bimolecular reactions of cyclohexenes. Thus, ***ii*** gives rise to the *major* isomers from **1** and **2** and the *minor* isomer from **3**. These results formulated two mechanistic questions: *1*) why does the sense of electrocyclization change as a function of substituent location and *2*) why does the major reaction pathway for **1** and **2** proceed *via* energetically unfavorable intermediates (and presumably transition states)?

The validity of the second question, *i.e.*, the importance of considering the relative energy of intermediates in predicting the outcome of charged electrocyclic processes is well established [6]. We assumed that ***ii*** is energetically less favorable than ***i***[7]). This assumption could be tested by approximation in the dissolving metal reduction of **8** *(Scheme 5)*. Current theory [7] predicts that the stereochemical outcome of these re-

Scheme 5



ductions is determined by the relative energy of radical anions related to ***iii*** and ***iv*** which are in rapid equilibrium. It is clear that ***iii*** and ***iv*** do not exactly model ***i*** and ***ii***, nonetheless they do embody the fundamental difference between the stereochemical families. Li/NH_3 reduction of **8** gave a ternary mixture of isomers of dihydro-**5**. The composition of the mixture (by capillary GC) demonstrated that ***iii*** is more favorable than ***iv*** (by a factor of 10) and suggests, as expected, that ***i*** should be more favorable than ***ii***, leading to the *cis*-family of isomers. Since this is not the case, other factors must be responsible for the observed outcome.

In all examples, the major isomers belonged to the *trans*-family. This corresponds to approach of the vinylsilane to the sterically more accessible face of the C(2')–C(3') double bond. The hypothesis that steric approach control is stereodetermining could be tested by changing the bulk of the R-groups. However, with general synthetic applicability in mind, a more ideal test (solution) is to *introduce a steric bias in the transition state, but not the product.* This is, in principle possible by changing the ligands on silicon[8]). For reasons of synthetic accessibility we selected the isopropyl group and synthesized the required substrates as outlined in *Schemes 6* and *7*. Hydrostannylation of triisopropylsilylacetylene (**9**) proceeded only under forcing conditions to give an

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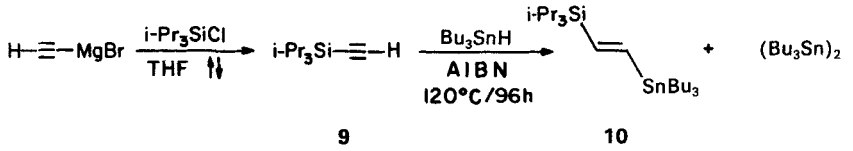
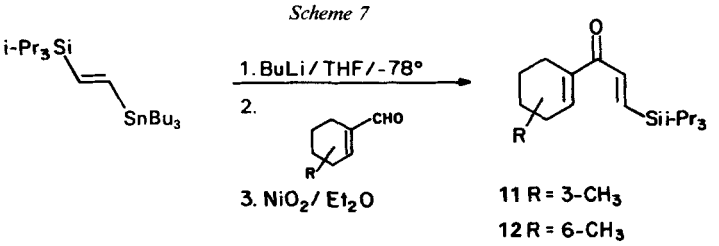
[7]) This may not be the case for $R=CH_3$ where **i** suffers from $A^{1,3}$ strain.

[8]) We explored the use of the stereoisomeric (*Z*)-vinylsilane from **3** only to discover instantaneous isomerization to the (*E*)-isomer under the reaction conditions.

Scheme 6



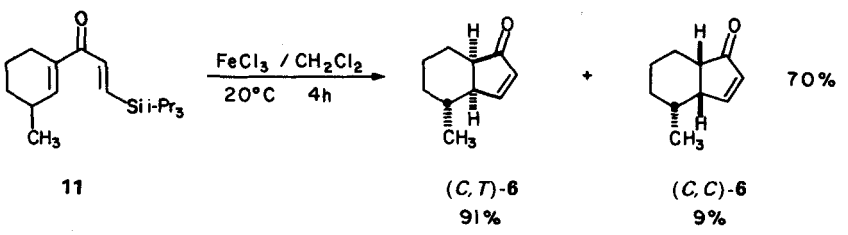
Scheme 7



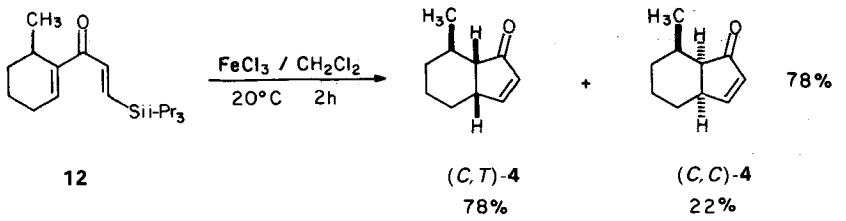
inseparable 4:1 mixture of **10** and hexabutyldistannane which was used as such. Transmetallation [8] with BuLi and addition of the vinyllithium species to 3- or 6-methyl-1-cyclohexenecarbaldehyde proceeded smoothly in 65 and 66% yields, respectively. The divinyl ketones **11** and **12** were obtained in 75 and 81% yields, respectively from the oxidation of the corresponding diallyl alcohols.

Substitution of isopropyl for methyl in β-silyl-substituted divinyl ketones has a rate-retarding effect: no reaction was observed at 0° with $FeCl_3$ *(Scheme 8)*. Reaction of **11** occurred cleanly (albeit in lower yield) at 20° to produce a mixture of (*C*,*T*)-**6** and (*C*,*C*)-**6** in a ratio of 91:9 which compares favorably to the 78:22 ratio observed for a β-Me_3Si-group. Only a fractional change was observed, however, in the cyclization of **12** *(Scheme 9)* which resulted in a 78:22 (*vs.* 72:28) ratio of (*C*,*T*)-**4** to (*C*,*C*)-**4**. Thus, the mechanistic picture most consistent with the stereochemical results invokes an early transition state for the cyclization in which the stereochemical family is established by the sterically more favorable approach of the vinylsilane to the internal double bond. This explanation is consistent with the stereoselectivity observed by *Hiyama et al.* [9] in the related *Raphael-Nazarov* cyclization. Direct comparison is difficult due to the presence of overriding steric interactions. Further, *Schultz* and co-workers [10] have concluded that a similar state-of-affairs obtains the conrotatory 6π-electrocyclization of α-aryloxyenones.

Scheme 8



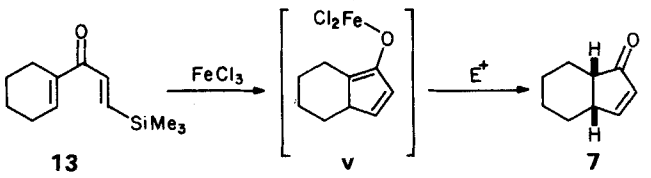
Scheme 9



12 (C,T)-4 78% (C,C)-4 22%

Iron Intermediates. – *Results and Discussion.* We have thus far considered intermediates only prior to or directly resulting from $FeCl_3$ induced cyclization. Loss of the silyl electrofuge should produce a cross-conjugated iron enolate ***v*** *(Scheme 10)*. There

Scheme 10



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exists only indirect evidence for such an intermediate. A full equiv. of $FeCl_3$ is desirable for best results, but as little as 0.4 equiv. are still effective (CH_2Cl_2/20°/1 h, 78%). Importantly, the reaction does not go to completion with 0.1 equiv., ruling out the intermediacy of silyl enol ethers. Furthermore, the isolation of *Michael*-addition products in acyclic cases and the apparent kinetic control of stereochemistry implicate a metallo-enolate. On the other hand, no products arising from oxidative coupling, an important reaction for iron(III) enolates [11], have been detected. Furthermore, we have been unable to trap the putative ***v*** from **15** with electrophiles such as Me_3SiCl, CH_3I, CH_3COCl, and $ClCO_2Et$[9]). In all cases only the parent hexahydro-2-inden-1-one **7** was obtained. Most disturbing, however, was the lack of deuterium incorporation when the reaction was worked up with D_2O and D_2O/NaCl. Suspicious of the 'anhydrous' $FeCl_3$ being used, we repeated the reaction under scrupulously anhydrous conditions using 99.99% $FeCl_3$. To our surprise, the reaction did not work; educt was consumed producing a myriad of products from which **7** could be present (if at all) only in trace amounts. The reaction could be turned on again however, by adding 1.5 equiv. of D_2O to the $FeCl_3$ prior to addition of the divinyl ketone **13**. In this way **7** was obtained in reasonable yield and was regiospecifically deuterated (75% D, by ^{1}H-NMR and MS) at C(7a).

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[9]) Of all the electrophiles tested only $ClCO_2Et$ was shown to give a stable O-derivative from the cross-conjugated lithium enolate. Methylation (CH_3I) of that enolate at C(7a) proceeded in 80% yield.

While several explanations of this behavior can be entertained, at the present time we favor that which invokes a stable hydrate of $FeCl_3$ ($FeCl_3 \cdot xH_2O$)[10])[11]) as the actual reagent. The intermediacy of **v** is necessary from the stoichiometry, but this species must be extremely reactive and can decompose by several pathways (redox or nucleophilic) unless it is immediately quenched. The ability of $FeCl_3$ to both induce cyclization and carry the quenching electrophile makes it the ideal reagent. The failure of $SnCl_4$, $AlCl_3$, $BF_3 \cdot OEt_2$ and $TiCl_4$ in earlier experiments may be attributed in part to the true anhydrous nature of these reagents[12]).

In summary, the effects of remote substituents on the stereochemical course of silicon-directed *Nazarov* cyclizations can be predicted in terms of steric approach control in the formation of the new C–C-bond. Good selectivity can be obtained with sterically demanding ligands on silicon and when the substituent is near the β'-terminus of the divinyl ketone. The necessity for stoichiometric amounts of water in the reaction mixture has been demonstrated. The application of this reaction to the synthesis of hydroazulene natural products is being pursued in these laboratories and will be reported in due course.

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Experimental Part

General. For a description of general experimental procedures and specifications see preceding paper. The HPLC analyses were done using a 25 × 4.5 mm column of silica gel (5 μm) with a flow rate of 2.0 ml/min and detection at 215 nm. Gas chromatographic analyses employed two columns: column A) 23 m of *OV-101 WCOT*, split ratio 30:1, flow rate: 1 ml/min (H_2); column B) 6% *OV-101* on 60–80 acid-washed *Chromosorb W* (12 ft × 1/8 in), flow rate: 30 ml/min (N_2). High-resolution and capillary-GC mass spectra were obtained on a *Varian MAT-731* spectrometer. 3-Methyl- and 6-methyl-1-cyclohexenecarbaldehyde [13] [14] were prepared by literature methods. High-purity (99.99%) $FeCl_3$ was obtained from *Cerac;* Milwaukee, Wisconsin and handled in a glove bag.

Cyclizations of Divinyl Ketones. – Reactions of **1**, **2**, **3**, **13** and **14** with $FeCl_3$ were done as described in the prec. paper *(Sect. 6)* with the modification in the cases of **13** and **14** that the reactions were done at 20°.

Cyclization of **1**. – *7β-Methyl-3aβ,4,5,6,7,7aβ-hexahydro-1* H-*inden-1-one* ((C,T)-**4**) *and 7β-Methyl-3aα,4,5,6,7,7aα-hexahydro-1* H-*inden-1-one* ((C,C)-**4**). Yield 85%, b.p. 110°/0.03 Torr, R_f 0.30 (hexane/EtOAc 4:1). HPLC analysis (50:10:0.5 hexane/CH_2Cl_2/CH_3CN) t_R 6.8 min (28%, (*C,C*)-**4**) and 7.6 min (72%, (*C,T*)-**4**). IR: 3020*m*, 2940*m*, 2870*m*, 1708*s* (C=O), 1458*w*, 1378*w*, 1340*w*, 1215*s*, 1208*s*, 930*w*. ^{1}H-NMR (360 MHz): 7.54 (*dd*, *J* = 5.6, 2.5, 1 H, H–C(3) both isomers); 6.13 (*d*, *J* = 5.2, 0.25 H, H–C(2) (*C,C*)); 6.10 (*dd*, *J* = 5.6, 2.0, 0.75 H, H–C(2) (*C,T*)); 3.09 (*m*, 0.25 H, H–C(3a) (*C,C*)); 2.96 (*m*, 0.75 H, H–C(3a) (*C,T*)); 2.41 (*dd*,

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[10]) Ferric chloride forms stable hydrates with 2, 2.5, 3.5 and 6 water molecules of hydration [12a].

[11]) In all preparative experiments we used 98% $FeCl_3$ (*Aldrich* or *Alfa-Ventron*) from the same bottle reproducibly over many months.

[12]) With the exception of $TiCl_4$ these reagents also form stable hydrates which have not been investigated: $AlCl_3$ [12b]; BF_3 [12c]; $SnCl_4$ [12d].

J = 5.5, 6, 0.25 H, H–C(7a) (*C,C*)); 2.02 (*dd*, J = 8.7, 2.8, 0.75 H, H–C(7a) (*C,T*)); 1.85–1.35 (br. *m*, 7 H, 3 CH_2 and H–C(7) both isomers); 1.24 (*d*, J = 7.0, 0.75 H, CH_3–C(7) (*C,C*)); 1.13 (*d*, J = 6.5, 2.25 H, CH_3–C(7) (*C,T*)). MS (70 eV): 150 (51, M^+), 135 (27), 122 (11), 121 (17), 109 (10), 108 (44), 107 (24), 96 (15), *95* (100), 94 (18), 93 (22), 91 (18), 83 (12), 82 (32), 81 (20), 80 (12), 79 (41), 77 (25), 68 (18), 67 (29), 66 (24), 65 (16), 55 (18), 53 (29), 52 (10), 51 (14). HR-MS[13]): $C_{10}H_{14}O$, calc. 150.1045; obs. 150.1044.

$C_{10}H_{14}O$ (150.22) Calc. C 79.96 H 9.39% Found C 79.24 H 9.52%

This mixture was hydrogenated according to the general procedure (prep. paper, *Sect. 6.1*). Yield 96%. GC analysis column A (100° (3 min), 5°/min, 120°), t_R 4.55 min (28%, (*C,C*)-H_2-**4**) and 4.85 min (72%, (*C,T*)-H_2-**4**). The mixture of perhydroindanones was subjected to MeONa-equilibration (prec. paper, *Sect. 6.2.1*) to afford a four component mixture; GC analysis column A (100° (3 min), 5°/min, 120°): t_R 4.26 min (23%, (*T,C*)-H_2-**4**), t_R 4.61 min (5%, (*C,C*)-H_2-**4**), t_R 4.92 min (70%, (*C,T*)-H_2-**4**) and t_R 6.85 min (2%, (*T,T*)-H_2-**4**). Capillary GC-MS gave a molecular ion for the first three components (m/z = 152), in addition to common ions at m/z = 83, 95, 108, 123, 137. The fourth component gave too few ions to be detected.

Cyclization of **2**. – *5β-*tert*-Butyl-3β,4,5,6,7,7aβ-hexahydro-1* H*-inden-1-one* ((C,T)-**5**) *and 5β-*tert*-Butyl-3aα,4,5,6,7,7aα-hexahydro-1* H*-inden-1-one* ((C,C)-**5**). Yield 82%, b.p. 100°/0.05 Torr, R_f 0.35 (hexane/EtOAc 4:1). HPLC analysis[14]) (50:10:0.5 hexane/CH_2Cl_2/CH_3CN), t_R 8.1 min (25%, (*C,C*)-**5**) and 9.6 min (75%, (*C,T*)-**5**). IR: 3010*m*, 2960*s*, 2875*s*, 1700*s* (C=O), 1585*m*, 1478*m*, 1470*m*, 1448*m*, 1395*m*, 1368*s*, 1342*w*, 1310*w*, 1290*w*, 1225*m*, 1215*m*, 1210*m*, 1195*m*, 928*w*, 865*w*. ^{1}H-NMR (220 MHz): 7.69 (*dd*, J = 5.4, 2.8, 0.75 H, H–C(3) (*C,T*)); 7.55 (*dd*, J = 5.3, 2.2, 0.25 H, H–C(3) (*C,C*)); 6.18 (*dd*, J = 5.3, 1.0, 0.75 H, H–C(2) (*C,T*)); 6.11 (*dd*, J = 5.4, 1.0, 0.25 H, H–C(2) (*C,C*)); 3.23–3.18 (*m*, 0.75 H, H–C(3a), (*C,T*)); 2.94–2.89 (*m*, 0.25 H, H–C(3a) (*C,C*)); 2.34 (*q*, J = 6, 0.75 H, H–C(7a) (*C,T*)); 2.30 (*q*, J = 6, 0.25 H, H–C(7a) (*C,C*)); 2.04-0.87 (br. *m*, 7 H, 3 CH_2 and H–C(5) both isomers); 0.81 (*s*, 9 H, $(CH_3)_3$C–C(5), both isomers). MS (70 eV): 192 (17, M^+), 137 (19), 136 (57), 107 (14), 95 (64), 82 (18), 79 (12), *57* (100), 55 (11).

$C_{13}H_{20}O$ (192.33) Calc. C 81.20 H 10.48% Found C 81.10 H 10.55%

This mixture was hydrogenated according to the general procedure. Yield 99%. GC analysis column A (120° (2 min), 10°/min, 160° (5 min)), t_R 5.63 min (24%, (*C,C*)-H_2-**5**) and 6.02 min (76%, (*C,T*)-H_2-**5**). The mixture of perhydroindanones was subjected to MeONa-catalyzed equilibration to afford a ternary mixture of isomers. GC analysis (as above): t_R 5.54 min (20%, (*C,C*)-H_2-**5**), t_R 5.78 min (4%, (*C,C*)-H_2-**5**) and t_R 5.90 min (76%, (*C,T*)-H_2-**5**). The identity of these isomers was assured by coinjection with an authentic sample from the Li/NH_3-reduction of **8**.

Cyclization of **3**. - *4α-Methyl-3aα,4,5,6,7,7aα-hexahydro-1* H*-inden-1-one* ((C,T)-**6**) *and 4α-Methyl-3aβ,4,5,6,7,7aβ-hexahydro-1* H*-inden-1-one* ((C,C)-**6**). Yield 99%, b.p. 100°/0.05 Torr, R_f 0.38 (hexane/EtOAc 4:1). GC analysis column A[15]) (100° (3 min), 5°/min, 120°), t_R 7.3 min (78%, (*C,T*)-**6**) and 8.0 min (22%, (*C,C*)-**6**). IR: 3030*w*, 3018*w*, 2960*m*, 2930*m*, 2870*w*, 1705*s* (C=O), 1630*w*, 1460*w*, 1390*w*, 1220*w*, 1158*w*, 882*w*. ^{1}H-NMR (360 MHz): 7.84 (*dd*, J = 5.8, 2.7, 0.75 H, H–C(3) (*C,T*)); 7.72 (*dd*, J = 5.8, 2.2, 0.25 H, H–C(3) · (*C,C*)); 6.26 (*dd*, J = 5.8, 2.0, 0.25 H, H–C(2) (*C,C*)); 6.16 (*d*, J = 5.8, 0.75 H, H–C(2) (*C,T*)); 3.06–3.00 (*m*, 0.25 H, H–C(7a) (*C,C*)); 2.51 (*m*, 1 H, H–C(3a) (*C,T*) and H–C(7a) (*C,C*)); 2.39 (*m*, 0.75 H, H–C(7a) (*C,T*)); 2.05–1.98 (*m*, 1 H); 1.69–1.51 (br. *m*, 5 H), 1.27–1.10 (br. *m*, 1 H), 1.06 (*d*, J = 2, 3 H, CH_3–C(4) both isomers). MS (70 eV): 150 (29, M^+), 135 (17), 122 (15), 108 (14), 107 (15), 95 (68), 94 (12), 93 (10), 91 (16), 82 (19), 81 (22), 80 (11), 79 (93), 79 (12), 77 (65), 68 (12), 67 (29), 66 (48), 65 (17), 63 (11), 55 (40), 53 (24), 52 (14), 51 (18), 50 (13).

$C_{10}H_{14}O$ (150.22) Calc. C 79.96 H 9.39% Found C 79.99 H 9.40%

This mixture was hydrogenated according to the general procedure. Yield 87%. GC analysis column A[15]) (100° (3 min), 5°/min, 120°), t_R 6.9 min (78% (*C,T*)-H_2-**6**) and 7.5 min (22%, (*C,C*)-H_2-**6**). MeONa-catalyzed equilibration produced an additional component GC analysis (as above) t_R 6.63 min (34%, (*T,T*)-H_2-**6**), t_R 6.89 min (45%, (*C,T*)-H_2-**6**) and t_R 7.45 min (21%, (*C,C*)-H_2-**6**). Capillary GC-MS measurement showed a strong molecular ion for each component (m/z = 152) as well as common ions m/z = 55, 67, 83, 95, 108, 123.

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[13]) Despite repeated purifications satisfactory combustion data could not be obtained.

[14]) Flow rate: 2.2 ml/min.

[15]) Flow rate: 0.9 ml/min, split ratio = 40:1.

5-tert-Butyl-2,3,4,5,6,7-hexahydro-1 H-inden-1-one (**8**). Prepared from 4-*tert*-butyl-1-cyclohexenecarboxylic acid chloride [15] by the method of *Magnus et al.* [16]. Yield 30%, b.p. 150°/0.1 Torr, m.p. 180–183°; sublimes 100°/0.2 Torr. GC analysis column A[14]) (100° (3 min), 5°/min, 120°): t_R 8.1 min. IR: 3025*m*, 2970*m*, 2870*m*, 1690*s* (C=O), 1650*s* (C=C), 1480*w*, 1470*w*, 1440*w*, 1425*w*, 1397*m*, 1368*m*, 1268*m*, 1220*m*, 1212*s*, 925*w*. ^{1}H-NMR (220 MHz): 2.48–1.91 (br. *m*, 10 H), 1.40–1.14 (br. *m*, 1 H), 0.91 (*s*, 9 H). MS (70 eV): 192 (21, M^+), 137 (10), 136 (68), 135 (18), 110 (10), 93 (11), 91 (17), 79 (17), *57* (100). HR-MS[15]): $C_{13}H_{20}O$, calc. 192.1514, obs. 192.1511.

Li/NH$_3$-Reduction of 8. – A solution of indenone **8** (88 mg, 0.30 mmol) in 1 ml of THF was injected into 5 ml of distilled NH_3 at −40°. Li metal was added in small pieces until a blue color persisted (*ca.* 5 mg, 0.72 mmol, 2.4 equiv.). The blue solution was stirred at −40° for 40 min and then quenched with solid ammonium chloride (0.1 g). After evaporation of the NH_3, the residue was partitioned between 10 ml each of H_2O and Et_2O and the aq. phase was separated and extracted with Et_2O again (3 × 20 ml). The individual Et_2O-extracts were washed with H_2O (3 × 15 ml) and brine (20 ml), then combined and dried over $MgSO_4$. Evaporation of the Et_2O left a residue (70 mg) which was analyzed on GC. GC analysis, column A (100° (3 min), 5°/min, 120°): four components: t_R 5.9 min (61%, (*C,C*)-H$_2$-**5**); t_R 60 min (13%, (*T,C*)-H$_2$-**5**); t_R 6.2 min (7%, (*T,T*)-H$_2$-**5**) and t_R 8.1 min (19%, **8**). The identity of these components was assumed by coinjection with the products of hydrogenation and equilibration of **5**.

Triisopropylsilylacetylene (**9**) [17]. Mg (1.21 g, 49.8 mmol) was suspended in 5 ml of THF in a 50-ml, 3-necked, round-bottomed flask fitted with reflux condenser and addition funnel under N_2. A solution of EtBr (5.42 g, 49.8 mmol) in 3 ml of THF was added dropwise and the mixture was refluxed for 1 h after complete addition. A sat. solution of acetylene in 40 ml of THF was prepared in a 250-ml, 3-necked, round bottomed flask fitted with a reflux condenser, rubber septum and gas-dispersion tube by bubbling acetylene (passed through in series a −78° cold trap, conc. H_2SO_4 and a K_2CO_3-tower) into the THF at r.t., then cooling to 0°, the ethyl magnesium bromide solution was added in 2-ml portions to the acetylene solution and the mixture was warmed to 25°. Introduction of acetylene was continued as chlorotriisopropylsilane (8.0 g, 41.5 mmol) was added dropwise. After complete addition, acetylene flow was stopped and the mixture was heated to reflux for 36 h. The reaction was quenched by the cautious addition of 750 ml of 1 N H_2SO_4 to the cold (0°) mixture. The aq. solution was extracted with Et_2O (3 × 100 ml) and the individual Et_2O extracts were washed with H_2O (2 × 80 ml) and brine (80 ml). The combined extracts were dried ($MgSO_4$) and concentrated on the rotavap. The crude product was contaminated with triisopropylsilanol which was removed by filtration through 40 g of silica gel with hexane. The final product was obtained by evaporation of the filtrate and distillation. Yield 65%, b.p. 100°/20 Torr. IR: 3025*s*, 3018*m*, 1520*w*, 1430*w*, 1218*s*. ^{1}H-NMR (220 MHz): 2.17 (*s*, 1 H, H−C(2)); 0.91 (*s*, 21 H, $((CH_3)_2CH)_3$−Si). MS (70 eV): 182 (8, M^+), 140 (10), 139 (66), 111 (67), 97 (29), *83* (100), 69 (66), 68 (11), 58 (11), 55 (14), 53 (13).

$C_{11}H_{22}Si$ (182.42) Calc. C 72.44 H 12.16% Found C 72.53 H 11.93%

(E)-2-*(Triisopropylsilylethenyl)-tributylstannane* (**10**). A neat solution of tributylstannane (5.58 g, 19 mmol), **9** (3.5 g, 19 mmol) and *ca.* 10 mg of 2,2'-azobisisobutyronitrile was heated at 120° for 96 h, at which point the stannane was consumed (GC). The resulting liquid was distilled and the distillate used for subsequent reactions. Yield 5.2 g, 64%, b.p. 135°/0.1 Torr. GC analysis column B (200° (2 min), 20°/min, 260° (15 min)), t_R 7.6 min (80%, **10**) and 8.9 min (20%, $(Bu_3Sn)_2$). ^{1}H-NMR (90 MHz); 7.03 (*d*, *J* = 23, 1 H); 6.47 (*d*, *J* = 23, 1 H); 2.0–1.2 (*m*, 18 H); 1.07 (*s*, 21 H); 0.89 (*t*, *J* = 7, 9 H).

Diallyl Alcohols from a Vinylstannane. – *General Procedure.* The mixture of stannanes **10** (1.18 g, *ca.* 2.4 mmol) was dissolved in 8 ml of dry THF and cooled to −78°. BuLi was added at −78° until **10** was consumed by GC analysis (1.2 equiv. BuLi/**10**). The resulting solution was warmed to −20°, maintained at −20° for 20 min, then cooled to −78°. The anion was quenched at −78° with the appropriate enal (1 equiv./equiv. BuLi in 1.0 ml THF) and the solution was warmed to 0°. H_2O (10 ml) was added, the mixture was extracted with Et_2O (3 × 20 ml), and the Et_2O-extracts were washed with 20-ml portions of H_2O and brine. Evaporation of the dried (K_2CO_3) Et_2O-layers gave a crude product which was purified by chromatography on silica gel and distillation.

(E)-*1-(3-Methyl-1-cyclohexenyl)-3-triisopropylsilyl-2-propen-1-ol.* Yield 65%, b.p. 130°/0.1 Torr, R_f 0.30 (hexane/EtOAc 8:1). IR: 3600*w* (OH), 3010*w*, 2960*s*, 2945*s*, 2890*s*, 2870*s*, 1618*w*, 1463*m*, 1382w, 1358*w*, 1215*w*, 1070*w*, 1018*w*, 997*m*, 910*w*, 882*m*. ^{1}H-NMR (220 MHz): 6.04 (*dd*, *J* = 19.1, 4.6, 1 H, H−C(3)); 5.76 (*dd*, *J* = 19.1, 1.0, 1 H, H−C(2)); 5.59 (*m*, 1 H, H−C(2')); 4.49 (*m*, 1 H, H−C(1)); 2.25–1.61 (br. *m*, 7 H, 3 CH_2 and H−C(4')); 1.04 (*m*, 24 H, CH_3−C(3') and $((CH_3)_2CH)_3$Si). MS (70 eV): 308 (4, M^+), 266 (22), *265* (100), 131 (15), 103 (27), 95 (13), 75 (53), 61 (42), 58 (24).

$C_{19}H_{36}OSi$ (308.64) Calc. C 73.95 H 11.76% Found C 74.02 H 11.87%

(E)-*1-(6-Methyl-1-cyclohexenyl)-3-triisopropylsilyl-2-propen-1-ol.* Yield 66%, b.p. 135°/0.04 Torr, R_f 0.30 (hexane/EtOAc 8:1). IR: 3600*w* (OH), 3020*m*, 2960*s*, 2945*s*, 2870*s*, 1618*w*, 1455*m*, 1382*w*, 1318*w*, 1235*m*, 1210*m*, 1065*w*, 998*m*, 885*m*. ^{1}H-NMR (220 MHz): 6.48–6.12 (*m*, 1 H, H–C(3)); 5.96–5.68 (br. *m*, 2 H, H–C(2) and H–C(2')); 4.63–4.52 (br. *m*, 1 H, H–C(1)); 2.45–1.05 (br. *m*, 35 H). MS (70 eV): 308 (3, M^+), 266 (21), *265* (100), 247 (23), 131 (25), 116 (11), 103 (32), 91 (10), 89 (12), 87 (13), 75 (58), 73 (20), 61 (46), 59 (42).

$C_{19}H_{36}OSi$ (308.64) Calc. C 73.95 H 11.76% Found C 73.72 H 11.74%

Oxidation of 2-Propen-1-ols. – The alcohols were oxidized with nickel peroxide according to the general procedure in the prec. paper *(Sect. 5)*.

(E)-*1-(3-Methyl-1-cyclohexenyl)-3-triisopropylsilyl-2-propen-1-one* (**11**). Yield 81%, b.p. 140°/0.01 Torr. IR: 3025*m*, 3018*m*, 2980*s*, 2945*s*, 2870*s*, 1643*s* (C=O), 1630 sh, 1580*m*, 1463*m*, 1385*w*, 1370*w*, 1263*m*, 1232*s*, 1210*s*, 1138*w*, 1070*w*, 1060*w*, 1032*w*, 1018*w*, 1000*m*, 968*w*, 930*w*, 910*m*, 882*m*, 790*s*. ^{1}H-NMR (220 MHz): 7.10 (*d*, *J* = 19.2, 1 H, H–C(2)); 7.02 (*d*, *J* = 19.2, 1 H, H–C(3)); 6.71 (*m*, 1 H, H–C(2')); 2.42 (br. *m*, 3 H, H–C(3') and 2 H–C(6')); 1.85–1.71 (br. *m*, 4 H, 2 H–C(4') and 2 H–C(5')); 1.30–0.99 (br. *m*, 24 H, CH_3–C(3') and $((CH_3)_2CH)_3Si$). MS (70 eV): 264 (24), 263 (100, $M^+ - 43$), 221 (26), 179 (13), 131 (13), 123 (11), 105 (10), 95 (24), 75 (32), 67 (14), 59 (21), 55 (11).

$C_{19}H_{34}OSi$ (306.62) Calc. C 74.44 H 11.18% Found C 74.58 H 11.40%

(E)-*1-(6-Methyl-1-cyclohexenyl)-3-triisopropylsilyl-2-propen-1-one* (**12**). Yield 75%, b.p. 150°/0.01 Torr. IR: 3020*s*, 2960*s*, 2945*s*, 2890*m*, 2870*s*, 1640*s* (C=O), 1630*m*, 1580*w*, 1465*m*, 1422*w*, 1385*w*, 1358*w*, 1260*m*, 1230*s*, 1220*s*, 1210*s*, 1080*w*, 1070*w*, 1000*m*, 968*w*, 910*w*, 882*m*. ^{1}H-NMR (220 MHz): 7.04 (*s*, 2 H, H–C(2) and H–C(3)); 6.78 (*m*, 1 H, H–C(2')); 2.87 (*m*, 1 H, H–C(6')); 2.24 (*m*, 2 H, 2 H–C(3')); 1.69–1.51 (*m*, 4 H, 2 H–C(4') and 2 H–C(5')); 1.23–0.97 (br. *m*, 24 H, CH_3–C(6') and $((CH_3)_2CH)_3Si$). MS (70 eV): 306 (2, M^+), 264 (23), *263* (100), 221 (20), 123 (10), 95 (15), 75 (24), 67 (12), 61 (15), 59 (22).

$C_{19}H_{34}OSi$ (306.62) Calc. C 74.44 H 11.18% Found C 74.14 H 11.39%

Cyclization of 11. – Yield 70%. GC analysis, column A[14]) (100° (3 min), 5°/min, 120°), 91% (*C,T*)-**6** and 9% (*C,C*)-**6** by coinjection with authentic material.

Cyclization of 12. – Yield 78%. HPLC analysis (50:10:0.5 hexane/CH_2Cl_2/CH_3CN), 22% (*C,C*)-**4** and 78% (*C,T*)-**4** by coinjection with authentic material.

Cyclization of 13 with $FeCl_3 \cdot D_2O$. – cis-*[7a-$^2H_1$]-3a,4,5,6,7-Pentahydro-1* H-*inden-1-one* (*[$^2H_1$]*-**7**). $FeCl_3$ (99.99%, 115 mg, 0.71 mmol) was transferred in a glove bag under N_2 into a flame-dried, 100-ml round-bottomed flask fitted with a 3-way stopcock. The stopcock was fitted with a rubber septum and attached to a N_2-line (P_2O_5 dried). Freshly distilled (CaH_2) CH_2Cl_2 (1.5 ml) was added followed by 18 µl of D_2O (99.8%, 0.99 mmol). The suspension was cooled to 0° and a solution of **15** in 0.5 ml of CH_2Cl_2 was added in one portion. After stirring at 0° for 4.5 h 5 ml of H_2O was added and the product was isolated and purified in the usual manner to afford [$^2H_1$]-**7** in 62% yield. The ^{1}H-NMR spectrum (220 MHz) was identical to **7** with the exception that the resonance at 2.40 (H–C(7a)) was only 25% of normal intensity (*ca.* 75% [$^2H_1$]). FDMS[16]): ratio of corrected peak areas for *m/z* 136 ÷ *m/z* 137 = 0.357, thus 74% [$^2H_1$].

[16]) The normal electron impact (EI) mass spectrum showed $M^+ + 1$, M^+, and $M^+ - 1$ peaks. The FDMS of **7** showed $M^+ + 1$, 6.8% of M^+ which allowed calculation of the ratio of **7**/[$^2H_1$]-**7** in this experiment.

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