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SILICON-DIRECTED NAZAROV CYCLIZATIONS VII
LINEARLY-FUSED TRICYCLICS

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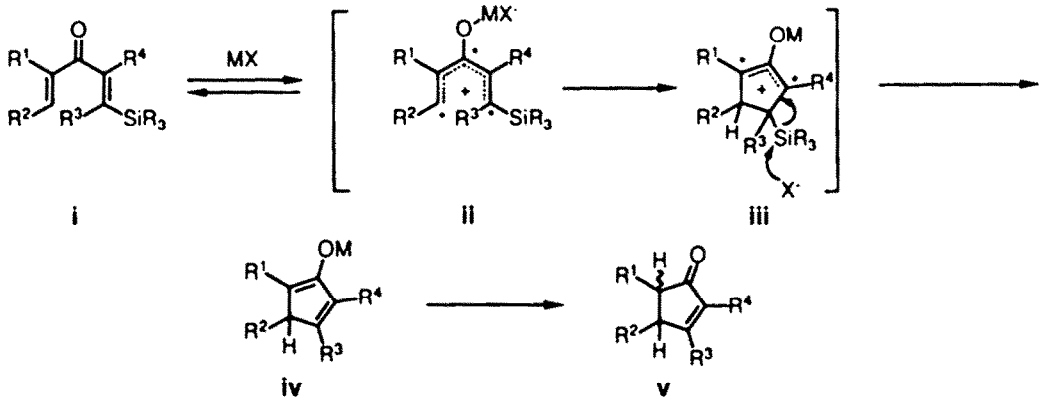
Abstract- A new modification of the silicon-directed Nazarov cyclization is described which involves the cyclization of divinyl ketones incorporating an allylsilane as the control unit. The cyclizations are extremely facile with $FeCl_3$ or $BF_3{\cdot}OEt_2$ as the Lewis acid. Four permutations of five- and six-membered ring substrates have been examined. In all cases the reactions are regio- and stereoselective. In the 6-5-6 (6aa) and 5-5-6 (6ba) systems the major product has the *trans-anti* configuration. The ability to incorporate a methyl substituent on the double bond and in the ring has been addressed.

INTRODUCTION

Previous reports from these laboratories have established the silicon-directed Nazarov cyclization (SDNC) as a mild and general method for the annelation and construction of cyclopentenones (Scheme 1).[2] The hallmark of the SDNC is the

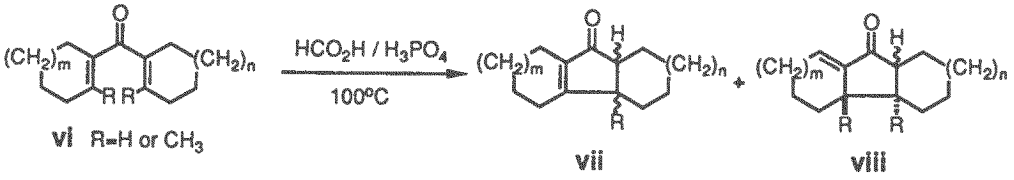
Scheme 1



exclusive formation of the thermodynamically less stable cyclopentenone isomer as predicted by the silicon-directed collapse of the intermediate cyclopentenyl cation **iii**. The controlled placement of the double bond away from the ring fusion allows the pericyclic nature of the reaction to be stereochemically expressed. We have extensively examined the consequences of the two different, allowed conrotations with regard to relative asymmetric induction with chiral substrates as a function of ring size (5, 6, 7 and 8), ring substituent position and size and silicon group size.[2c,2d,2e] In addition, recent studies have demonstrated a wide functional group compatibility (olefins, ethers, esters, carbamates) for the reaction.[2d] Further, from the effects of double bond substituents on rate, these studies have provided strong support for the mechanism involving a rate determining electrocyclization of cation **ii** to cation **iii**.

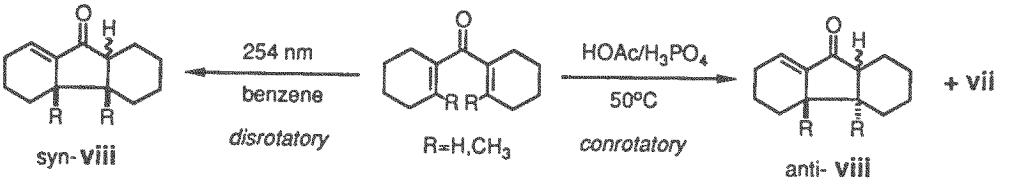
Continuing our investigations on the structural versatility of the SDNC we envisioned a new variant which would provide access to linear tricyclic compounds, Scheme 2. The classical Nazarov cyclization[3] has been only sparsely employed

Scheme 2



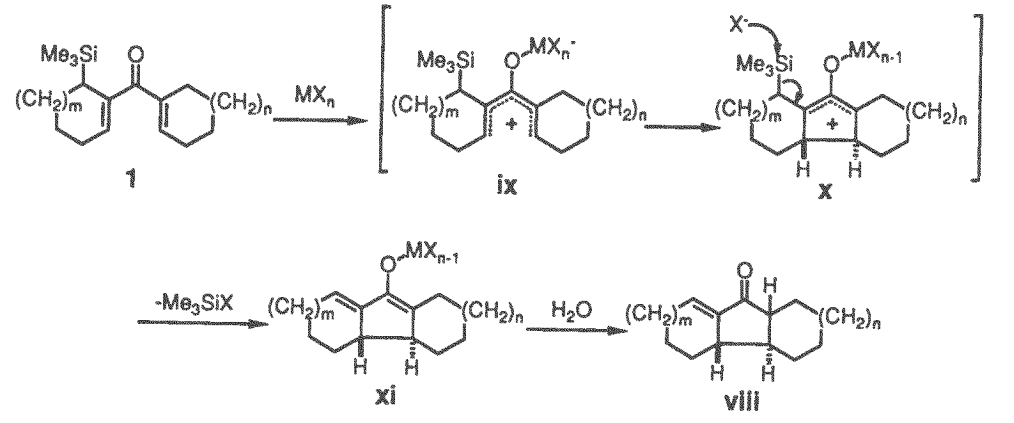
in the construction of these ring systems. The earliest reports, due to Braude[4], describe the production of 6-5-6 (vii R=H, m=n=1), 7-5-7 (vii R=H, m=n=2) and aromatic versions of these systems.[5] In more recent times, Eaton[6] and Mehta[7] have reported cyclizations leading to tri- and tetraquinanes via this route. In all of these examples the double bond takes up the (thermodynamically most stable) ring fusion position (→vii), most likely due to the severe reaction conditions (polyphosphoric acid/100°C). This, of course, cannot occur when the ring fusions are substituted as in the Harding[8] synthesis of trichodiene which is the only case of a 6-5-5 (viii R=Me, m=1, n=0) system constructed in this fashion. Despite the limited synthetic utility, it is this type of cyclization which is the most highly quoted example of the Nazarov cyclization. In their landmark treatise on the theory of electrocyclic reactions Woodward and Hoffmann cited the only experimental verification of the complementary rotatory pathways for electrocyclization of pentadienyl cations under thermal and photochemical conditions[9], Scheme 3. This was made possible by careful adjustment of the reaction conditions to allow

Scheme 3



formation of the required "exo-ketones" viii. The purpose of our present study was to apply the concept of silicon-directed collapse of cations to allylsilane systems of the type **1**, Scheme 4. Although no longer directly located on the divinyl ketone

Scheme 4



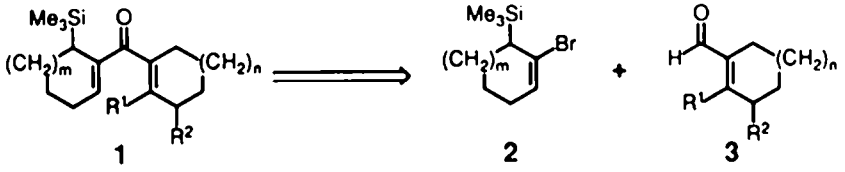
moiety, the silicon unit is perfectly disposed to direct the fate of the cyclopentenyl cation, **x**, after the key closure of **ix**. From our previous work and the well-known cation stabilizing effect of the silicon (β-effect)[10] we could *a priori* predict that these reactions should proceed much faster than the vinylsilane SDNC's (see **Discussion**). Furthermore, we hoped to gain stereocontrolled access to a number of tricyclic systems (by selective, kinetic protonation of **xi**)[11] especially the triquinanes which have been recently the subject of intense synthetic activity.[12]

RESULTS

A. *Preparation of β-Silyl Divinyl Ketones*

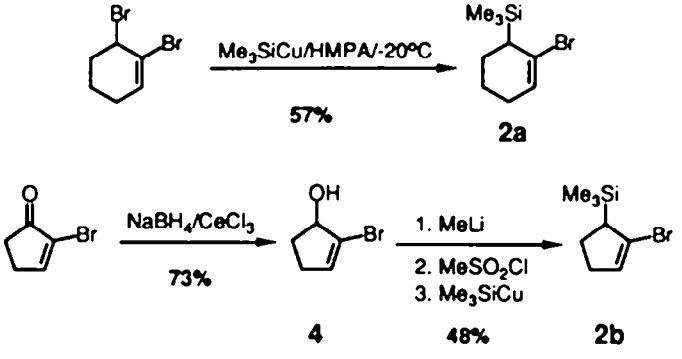
To maximize efficiency in the preparation of substrates with different ring sizes and substitution patterns we employed the route shown in Scheme 5. This disconnection required the preparation of the two allylsilanes **2a** and **2b**. For these

Scheme 5



simple allylsilanes the method of Smith[13] proved most effective, Scheme 6. Although initially troublesome, we found that the generation of the Me_3SiCu reagent could be made reproducible if the Me_3SiLi precursor was formed by cooling the HMPA/Me_6Si_2 solution from 8°C to -20°C as the MeLi was being added. Using this procedure **2a** could be obtained from 2,3-dibromocyclohexene[14a] in one step. The next lower homolog **2b** was obtained in similar fashion from the in-situ-prepared mesylate of 2-bromo-2-cyclopentenol, itself prepared by Luche reduction[15] of the known bromo ketone[14b]. The

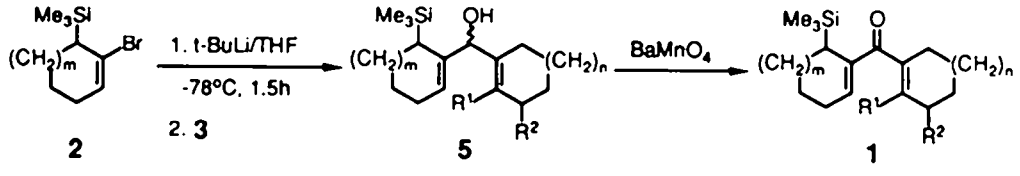
Scheme 6



requisite aldehydes **3a-d** were obtained using literature procedures.

The two components were coupled via the vinyllithium reagents obtained from **2a** and **2b**. Following the general procedure described by Seebach[16] the Br/Li exchange with *t*-BuLi required *ca.* 1.5 h at -78°C. Addition to the aldehydes proceeded cleanly at -78°C to give the divinyl alcohols **5**. Oxidation of **5** with $BaMnO_4$ afforded the target ketones **1** with no detectable by-products, Scheme 7. The yields for these transformation are collected in Table 1.

Scheme 7



B. *Cyclization of β-Silyl Divinyl Ketones*

All of the five substrates underwent facile Nazarov cyclization with complete regiocontrol expressed by the trimethylsilyl unit. The reactions proceeded very rapidly as expected even for the five-membered ring substrates. For each divinyl ketone **1** we assigned the full stereostructure of the major products, identified all isolable reaction by-products and

investigated the effects of reaction conditions (Lewis acid, concentration, addition order). The results of these experiments will be described for each individual cyclization.

B.1. *Cyclization of 1aa*

The viability of the β'-silicon-directed Nazarov cyclization was demonstrated with **1aa** which would give a 6-5-6 ring

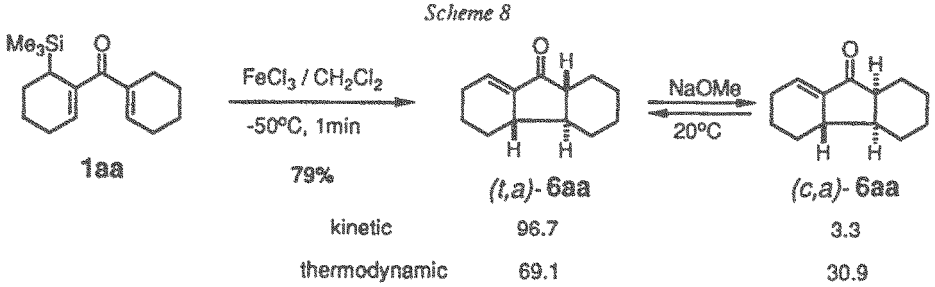
Table 1. Yields for alcohols **5** and ketones **1**.[a]

m	n	R^1	R^2	carbinol	yield, %	ketone	yield,%
1	1	H	H	**5aa**	70	**1aa**	71
1	0	H	H	**5ab**	72	**1ab**	88
0	1	H	H	**5ba**	77	**1ba**	70
0	0	H	H	**5bb**	78	**1bb**	80
0	0	CH_3	H	**5bc**	82	**1bc**	80
0	0	H	CH_3	**5bd**	75	**1bd**	78

[a] Yields of products after chromatography and distillation.

system. An initial survey of reaction conditions, which included the protocol previously established in our laboratories, revealed that the reaction was proceeding with $FeCl_3$ in CH_2Cl_2 very rapidly even at -30°C! Subsequent studies (*vide infra*) established the optimal conditions to involve an inverse addition of the substrate **1aa** to a slurry of $FeCl_3$ in CH_2Cl_2 at -50°C. Capillary GC analysis of the crude reaction mixture showed the presence of five components: A-E (increasing elution time) of which the major, A, was always present in >80%. This component could be efficiently isolated (79%) by distillation and recrystallization. Chromatography led to significant losses. Spectroscopic and elemental analysis of this product clearly identified it as the expected tricyclic compound **6aa** (Scheme 8). While we could assume that the two six-membered rings

Scheme 8



were *anti* related on mechanistic grounds (*vide infra*) the ring fusion configuration could not be assigned. An exhaustive literature search failed to provide any mention of the configurational assignment for this ring system despite its historical importance in the theory of electrocyclic reactions. The ultimate assignment of configuration rests on an X-ray structure determination of the thiosemicarbazone of the *trans-anti* isomer (*t,a*)[17] of **6aa** (mp 175-177°C) as reported in the Ph. D thesis of Dr. Roland E. Lehr.[9b] The minor isomer, also seen in reaction mixtures, was identified as *cis-anti* **6aa** ((*c,a*)-**6aa**) by epimerization of the *trans* ketone.

To assure that no epimerization occured *during derivatization* we prepared the thiosemicarbazones of both isomers. Thus ketone A was subjected to a base-catalyzed epimerization (NaOMe or KO*t*Bu) to afford a stable 69:31 mixture of A and B thereby establishing their isomeric relationship (Scheme 8). B was isolated from the mixture and each ketone was derivatized. The melting points of the derivatives were sufficiently distinct to assure the assignment of A as (*t,a*)-**6aa**

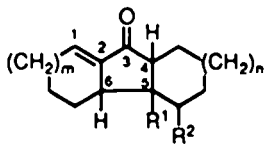


Table 2. Selected Spectroscopic Data for 6.[a]

compound	m	n	R^1	R^2	IR,cm^{-1} ν_{CO}	IR,cm^{-1} ν_{CC}	^{1}H-NMR, δ H-C(1)	^{13}C-NMR, δ[b] C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
(*t,a*)-**6aa**	1	1	H	H	1713	1653	6.67	131.5	141.0	204.7	54.9	42.4	48.1
(*c,a*)-**6aa**	1	1	H	H	1719	1649	6.71	133.4	141.0	207.7	48.4	37.0	40.2
(*c,a*)-**6ab**	1	0	H	H	1713	1651	6.50	131.6	142.7	209.6	52.8	42.7	46.5
(*t,a*)-**6ba**	0	1	H	H	1717	1630	6.48	133.7	149.9	201.9	61.1	50.8	52.3
(*c,a*)-**6bb**	0	0	H	H	1711	1634	6.41	133.5	151.2	205.3	58.7	47.7	53.0
(*c,a*)-**6bc**	0	0	CH_3	H	1711	1634	6.39	133.6	149.9	204.9	66.8	48.0	54.8
(*c,a*)-**6bd**[c]	0	0	H	CH_3	1711	1634	6.48-6.40	133.4 133.1	151.3 151.0	205.6 205.0	58.5 57.7	55.7 53.8	53.3 47.0

[a] Arbitrary numbering for all cyclization products as given in the parent structure. [b] Assignments aided by multiplicities from APT spectra. [c] Mixture of two C(5)-methyl epimers.

(thiosemicarbazone mp 169°C)[18] and B as (*c,a*)-**6aa** (thiosemicarbazone mp 199.5°C). Comparison of the relevant spectroscopic data for the cyclization products is collected in Table 2.

The large kinetic preference for the *trans-anti* over the *cis-anti* isomer was surprising in light of the usual *cis* ring fusion preference we have observed in SDNC products.[2] This does not arise from a strong thermodynamic preference in the products as shown by the equilibrium energy difference of 0.47 Kcal/mol at 25°C which translates to a 74:26 ratio at -50°C. Molecular mechanics calculations (MM2) nicely corroborated this number with the following strain energies (Kcal/mol): (*t,a*)-**6aa**, 14.54 ; (*c,a*)-**6aa**, 14.90 (ΔE= 0.36).

The remaining three products from the cyclization, C-E, were tentatively assigned by GC-mass spectrometry, Table 3. Component C formed in 2-9% is an unidentified isomer of **6aa** possibly the "endo ketone", **vii**, (ring fusion double bond)

Table 3. Products from cyclization of **1aa**.

component	A	B	C	D	E
	(*t,a*)-**6aa**	(*c,a*)-**6aa**	**7**	**8**	**9**
$t_R$min	10.14	10.45	10.61	11.58	12.13
%	89.0	6.7	2.7	0.9	0.6
M^+	190	190	190	188	244

observed by Lehr[9b] as a major product. The next component D found in 1-4% is a dehydro-**6aa** which probably arises from component E or a common precursor. The molecular ion and isotope ratio for E leave little doubt that this material contains

chlorine. These kinds of oxidized by-products are not unexpected from reactions involving iron(III) enolates.[19] Our next studies addressed how to suppress their formation.

Two experimental variables were examined to optimize the reaction. In the first series of experiments the order of addtion of the $FeCl_3$ was changed from normal ($FeCl_3$ added to the ketone solution) to inverse (ketone added to a suspenison of $FeCl_3$). The results in Table 4 show that the the inverse addtion led to a faster reaction (-50°C, 1min) and a smaller sum total of by-products, especially the stereoisomers. The amount of oxidized by-products was found to be sensitive to the

Table 4. Optimization experiments with **1aa** and **1ab**.[a]

	addition order[b]		concentration, M[e]		
products	normal[c]	inverse[d]	0.08	0.02	0.0004
A	82.8	84.7	83.6	89.6	83.9
B	3.0	2.9	3.0	3.4	2.0
C	8.5	2.8	3.8	3.3	8.0
D	1.0	3.6	4.4	1.4	3.6
E	1.3	5.7	5.2	1.9	1.6
6ab	88.8	95.0	95.0	97.9	92.6
F	8.2	2.6	2.6	0.9	2.0

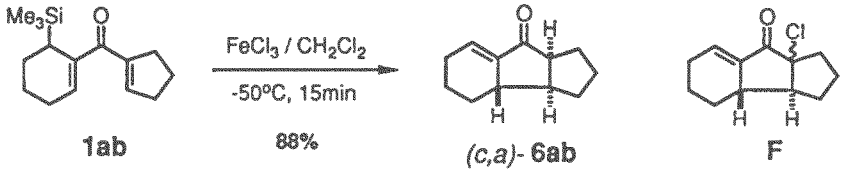
[a] All reactions run in CH_2Cl_2 with 1.05 equiv of $FeCl_3$. Data are absolute % of volatiles by GC analysis. [b] See text for explanation. [c] Reaction run at 0.08M at -30°C. [d] Reaction run at 0.08 M at -50°C. [e] All reactions run with inverse addition.

concentration of the reaction as shown in Table 4. Using the inverse addtion protocol the preferred concentration was found to be 0.02M At this concentration the reaction was still rapid at -50°C. At lower concentration the reaction had to be run at 0°C which led to a larger proportion of C.

B.2. *Cyclization of* ***1ab***

Nazarov cyclization of ketone **1ab** under the preferred reaction conditions described above was particularly noteworthy. The reaction proceeded at -50°C to give (*c,a*)-**6ab** as the major product (88% yield) along with a trace of a chlorinated by-product **F** (Scheme 9). No other stereoisomers could be detected. The assignment of structure for **6ab** derived readily from the spectroscopic data (Table 2). However, the assignment of configuration rested solely on the

Scheme 9



1ab (*c,a*)- **6ab** **F**

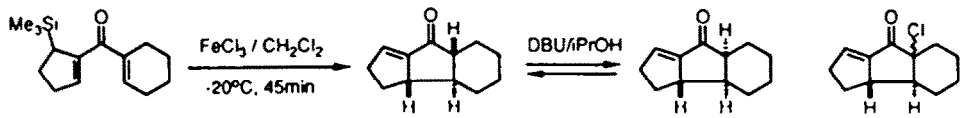
mechanistic imperative of conrotation and the large energy difference between *cis*- and *trans*-fused five-membered rings.[20] The structure of the by-product **F** was suggested by capillary GC-MS analysis which displays a molecular ion at m/z=210.

In optimization experiments (Table 4) this reaction was found to be sensitive to the order of addition of reagents but not to concentration. In the normal addition mode as much as 8% of **F** was formed. This could be nearly completely suppressed by inverse addition at any concentration.

B.3. *Cyclization of* **1ba**

In contrast to the results with **1ab**, we were unable to obtain high yields of cyclization products from **1ba**. The reactions proceeded rapidly at -20°C and GC analysis of the crude reaction mixtures (under optimal conditions) showed only the expected product **6ba**, along with a stereoisomer (vide infra) and a trace amount of a chlorinated by-product (**G**[21], Scheme 10. Isolation of the products, however, proved problematic as higher molecular weight materials (probably dimers)

Scheme 10



1ba	36%	*(t,a)*-**6ba**	*(c,a)*-**6ba**	**G**
	kinetic	96 6	3 4	
	thermodynamic	84.2	15.8	

appeared. The production of dimers was also capricious during the reaction. Optimization studies, Table 5, showed that the formation of these by-products was sensitive to both concentration and temperature (entries 1-4). The dimeric products were not derived from oxidative processes as they were also observed in reactions with BF_3OEt_2. With this, non-oxidizing, Lewis acid the formation of **G** was suppressed but even at 0.004M the dimers were formed. Furthermore, **6ba** was recovered unchanged from treatment with $FeCl_3$ under the reaction conditions.

The stereostructure of the major product was assigned as for **6aa** by comparison of thermodynamic stabilities of the *cis* and *trans* isomers. Attempted epimerization of **6ba** with NaOMe or KO*t*Bu led to facile conjugate addition of the base or

Table 5. Optimization experiments with **1ba**.[a]

entry	Lewis acid	conc., M	temp, °C	products, GC %				yield,[c] %
				(*t,a*)-**6ba**	(*c,a*)-**6ba**	**G**	dimers[b]	
1[d]	$FeCl_3$	0.08	-20	29.8	1.3	7.9	40	
2[d]	$FeCl_3$	0.02	-20→0	86.5	2.4	6.5	trace	36
3[d]	$FeCl_3$	0.004	-50→0	73.8	3.1	10.4	trace	
4[d]	$FeCl_3$	0.04	0	65.8	2.3	4.2	25	28
5[e]	BF_3-OEt_2	0.08	-10	35.1	1.9	0	45	9
6[e]	BF_3OEt_2	0.004	5	69.1	1.1	0	25	35

[a] Reactions run in CH_2Cl_2 with 1.05 equiv. of Lewis acid. [b] Sum of all peaks t_R >19 min. [c] Yield of **6ba** after chromatography. [d] Reverse addition. [e] Normal addition.

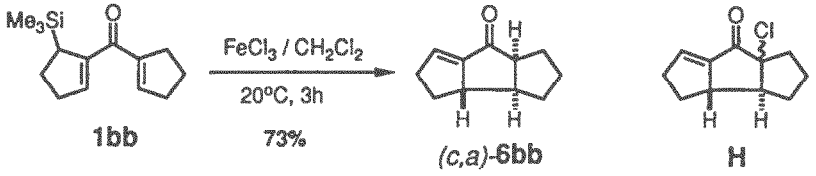
self-condensation. A clean epimerization could be effected with DBU in *i*PrOH (Scheme 10) to give an equilibrium ratio of 81.9:18.1 (ΔG= 0.90) still favoring the major component. Molecular mechanics calculations gave the following strain energies (Kcal/mol): (*t,a*)-**6ba**, 22.22; (*c,a*)-**6ba**[22], 23.05 (ΔE=0.83), thus allowing the assignment of the trans-anti configuration for the major isomer.

The difficulties observed in the epimerizations provided a clue to explain the poor yields of tricyclic products. The simultaneous capacity for facile conjugate addition and facile enolization combine to deplete the desired product. We have observed this behavior previously in the SDNC of acyclic divinyl ketones[2a]. Interestingly, the problem is not encountered with **6aa** or **6ab** because they are not as reactive Michael acceptors. It shoud be mentioned that **6ba** is stable for days at r. t. in the pure state.

B.4. *Cyclization of 1bb*

Three different substrates were examined which produce a linear array of five-membered rings. These substrates are obviously of interest in the synthesis of linear triquinane natural products. While the reactions could be run with either $FeCl_3$ or $BF_3{\cdot}OEt_2$ optimization was done only with the unsubstituted case **1bb**. This substrate reacted to give a single tricyclic product **6bb** which was assigned the *cis-anti* configuration as described for **6ab**, Scheme 11. As in the cyclization of **1ba**

Scheme 11



the major problem was the elimination of high molecular weight dimers which were formed at higher reaction concentration. The results of optimization experiments in Table 6 show that in this case the higher reaction temperature required for $BF_3{\cdot}OEt_2$ did not lead to higher precentages of dimeric products. Since oxidized by-products were completely absent, $BF_3{\cdot}OEt_2$ became the reagent of choice for this and the remaining substrates **1bc** and **1bd**. These cases were expected to cyclize slower than **1bb** and therefore the higher reaction temperatures preclude the use of $FeCl_3$.

B.5. *Cyclization of 1bc* and *1bd*

Having demonstrated the ability to construct linear triquinanes under mild condition and in high yield, we then sought to examine substrates which embodied structural features contained in various triquinane natural products. Two

Table 6. Optimization experiments with **1bb**.[a]

entry	Lewis acid	conc., M	temp, °C	products, GC, % (*c,a*)-**6bb**	**H**	dimers[b]	yield,[c] %
1[d]	$FeCl_3$	0.08	-20	57.9	10.4	29.7	
2[d]	$FeCl_3$	0.02	0	81.6	6.6	10.2	
3[d]	$FeCl_3$	0.004	-20	87.9	1	6.7	73
4[e]	$BF_3{\cdot}OEt_3$	0.08	0	70.5	0	21.0	
5[e]	$BF_3{\cdot}OEt_2$	0.004	0	96.5	0	3.5	
6[e]	$BF_3{\cdot}OEt_2$	0.004	10	88.6	0	8.4	77

[a] All reactions run in CH_2Cl_2 with 1.05 equiv. of Lewis acid. [b] Sum of all peaks t_R >19 min. [c] Yield of **6bb** after chromatography and distillation. [d] Reverse addition. [e] Normal addition.

common and very important features are angular methyl groups and ring substituents.

To incorporate an angular methyl group in the product we must be able to induce cyclization with a substrate bearing a methyl group on the C(β) atom. The presence of that methyl group in **1bc** was expected to slow the cyclization[2d] and indeed with BF_3OEt_2 the reaction took *ca.* 3 h (0.004M). Nonetheless, GC analysis of the reaction mixture showed only one product which was isolated in 78% yield, Table 7. The complete absence of dimers in this reaction may arise from the increased hindrance around the nucleophilic C-atom. Comparison of the spectroscopic data for (*c,a*)-**6bc** and (*c,a*)-**6bb** confirm the assignment of structure.

The presence of substituents in the peripheral rings introduces the problem of diastereoface selectivity (relative

asymmetric induction). Previous studies in our laboratories have shown that the level of selectivity is low in the SDNC's with five-membered rings[2c] bearing only a methyl group next to the reacting center. To investigate whether this carries over to

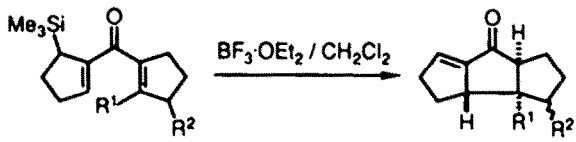


Table 7. Cyclization of **1bb**, **1bc** and **1bd**.[a]

substrate	R^1	R^2	temp, °C	time, h	product	yield,[b] %
1bb	H	H	10	0.25	(*c,a*)-**6bb**	77
1bc	CH_3	H	20	3.5	(*c,a*)-**6bc**	78
1bd	H	CH_3	10	1.0	(*c,a*)-**6bd**[c]	83

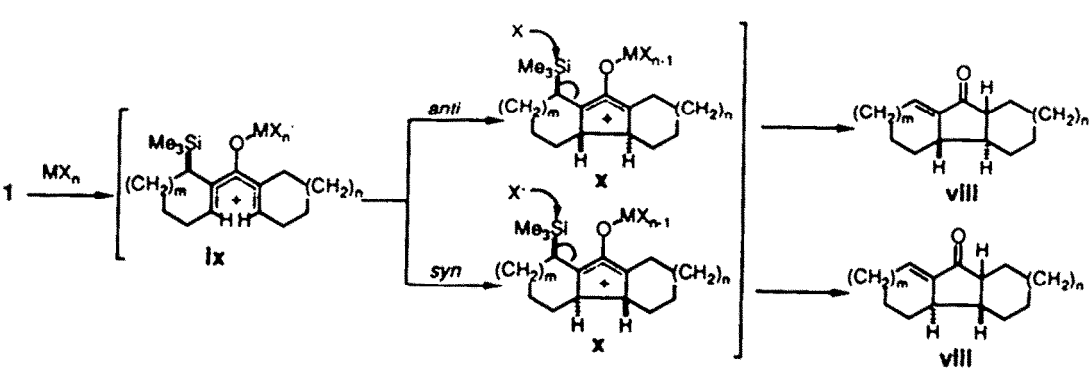
[a] All reactions were done in CH_2Cl_2 with 1.05 equiv of BF_3·OEt_2 at 0.02M by normal addition. [b] Yield after chromatography and distillation. [c] Formed as a 53:47 mixture of methyl epimers.

the construction of triquinanes, the substrate **1bd** was examined. Under the preferred conditions (BF_3·OEt_2/0.004M) cyclization occured cleanly to give **6bd** in 83% yield as a 53:47 mixture of two isomers, Table 7. That these were the two methyl epimers of (*c,a*)-**6bd** was easily seen in the similarity of the ^{13}C chemical shift for the carbonyl C(α) atoms and the dramatic difference in the chemical shifts of the methyl groups (Table 2). Thus, as before the methyl group was ineffective in controlling the sense of conrotation leading to the two diastereoisomers.

DISCUSSION

Certainly the most striking aspect of this variant of the SDNC is the dramatic rate enhancement. In the original vinylsilane variant, the silicon was found to weakly decelerate the reaction while completely directing the placement of the double bond.[2a] This is due to the fact that the hyperconjugative stabilization of the developing positive charge in cation **iii** is greatest when the silyl group is parallel with the π-system[10]; a situation which obtains only late on the reaction coordinate. In the examples described above, the location of the silyl moiety on an sp^3-carbon atom adjacent to the dienyl system allowed for continuous hyperconjugative overlap with attendant stabilization of the developing charge in cation **x** (Scheme 12). Not surprisingly, in these cases as well, the placement of the double bond was exclusively controlled by the departure of the silicon electrofuge. It is interesting to note that the substrates **1** , being chiral, can undergo two distinct conrotatory closures. The two pathways are diastereomeric and result in two different orientations of the silyl moiety with respect to the π-system in

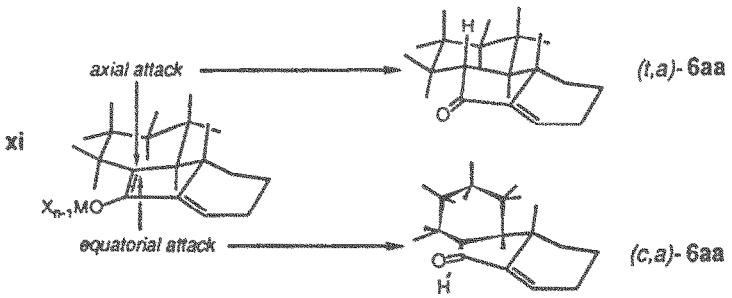
Scheme 12



cation x (Scheme 12). Since the silyl-bearing stereogenic center is destroyed, the products are enantiomeric. Thus an optically active sample of **1** is required to evaluate the extent of relative 1,3-asymmetric induction. While other factors are at play, the stereoelectronic preference for anti substitution in allylsilanes will certainly contribute.[23]

The second interesting feature of the cyclizations is the high kinetic selectivity observed in the protonation of the cross-conjugated metal dienolates **xi** (Scheme 13). In simple exocyclic enolates and enols steric approach control is usually cited to explain the predominantly equatorial protonation.[11,24a] Careful examination of molecular models failed to provide a

Scheme 13



clear bias for steric approach control in this reaction. The relatively rigid dienolate allows for a clear distinction between β-face (axial) and α-face (equatorial) approach, though in exocyclic enolates the stereoelectronic requirement is met by both routes.[24b] The high selectivity can be explained by comparison of the MM2 strain energies of the immediate products of protonation. Attack from the β-face produces the observed major isomer *trans,anti*-**6aa** (E=14.54 Kcal/mol). Attack from the α-face, however, leads to the *less stable conformer* of the minor isomer *cis,anti*-**6aa** (E=19.03 Kcal/mol) in which the carbonyl group is axial to the saturated ring. The ring-flipped conformer of *cis,anti*-**6aa** (E=14.90 Kcal/mol) is considerably more stable but cannot be directly accessed from **xi**.

In conclusion, a new variant of the SDNC which creates linear tricyclic systems has been documented. The reaction has been shown to possess good structural generality and proceeds with excellent degrees of regio- and stereocontrol. The preparation of **1aa** in optically active form and the application of this methodology to the synthesis of complex linear triquinanes is currently under investigation.

Experimental Part

General Data. - ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a *General Electric QE-300* (300 MHz ^{1}H, 75.5 MHz ^{13}C) in deuterochloroform with tetramethylsilane or chloroform (δ=7.26 ppm) as internal standard. Chemical shifts are given in ppm(δ) relative to TMS; multiplicities are indicated by *s* (singlet), *d* (doublet), *t* (triplet), *q* (quadruplet), *m* (multiplet), or br. (broadened). Coupling constants, *J*, are reported in Hz. Infrared spectra were obtained on an *IBM Instruments Inc. IR/32* FT-IR spectrometer. Peaks are reported in cm^{-1} with the following relative intensities: *s* (strong, 67-100%), *m* (medium, 66-34%), *w* (weak, 33-0%). Mass spectra were recorded on a *Varian MAT CH-5* Spectrometer with ionization voltages of 10 and 70 eV. Data are reported in the form *m/z* (intensity relative to base = 100). Elemental analyses were performed by the University of Illinois Microanalytical Services Laboratory.

Melting points (m.p.) were obtained on a *Thomas Hoover* capillary melting point apparatus and are corrected. Bulb-to-bulb distillations were performed using a *Buchi GKR-50 Kugelrohr*, with boiling points (b.p.) referring to air bath temperatures which are uncorrected. Analytical gas chromatography was performed on a *Varian 3700* Gas Chromatograph fitted with a flame ionization detector and programmable temperature control. Columns: packed, 3% Silicone OV-17 on 60-80 Chromosorb Q (6 ft by 1/8 in.); capillary, 5% silicone OV-17, 50 m. Retention times (t_R) and intergrals were obtained

from a *Hewlett Packard 3390A* recorder. Cuprous iodide was purified by the method of *Sum* and *Wieler*[25]. All reactions were performed in oven-dried (125°C) or flame dried apparatus under N_2 or Ar.

Starting Materials. - The following compounds were prepared by literature procedures: 2,3-dibromocyclohexene[14a], 2-bromo-2-cyclopentenone[14b], 1-cyclohexenecarbaldehyde (3a) [26], 1-cyclopentenecarbaldehyde (3b)[27], 2-methylcyclopentene-1-carboxaldehyde (3c)[28], 3-methylcyclopentene-1-carboxaldehyde (3d)[29].

Preparation of 2-Bromo-3-trimethylsilylcyclohexene (2a). To a solution of hexamethyldisilane (18.30 g, 125 mmol) in HMPA (100 ml) at 8°C under argon was added methyllithium (96.2 ml of a 1.3 M soln. in Et_2O, 125 mmol) dropwise as the reaction mixture was chilled to -20°C. After being stirred for 3 min, the resulting red soln. was treated rapidly with copper (I) iodide (23.80 g, 125 mmol) in dimethyl sulfide (50 ml), which caused the reaction mixture to rise rapidly in temperature. The resulting black soln. was cooled to -20°C and stirred for 3 min, and 2,3-dibromocyclohexene (12.0 g, 50 mmol) was added rapidly *via* syringe. The reaction mixture was warmed to r.t. and stirred 1 h. It was then poured into 500 ml of pentane and 500 ml of sat. NH_4Cl soln. (buffered to pH 8 by addition of NH_4OH), and the mixture was vigorously stirred for 3 h. The aqueous phase was extracted with two 500-ml portions of pentane, and the combined organic extracts were washed with H_2O and dried over magnesium sulfate, filtered, and concentrated. The crude product was chromatographed (hexane) and distilled. Yield 6.65 g (57%). B.p.: 82-83°C/7 Torr. R_f=0.51(hexane). GC: t_R = 3.95 min, COV-17; program: 130°C (3 min.), 20°C/min, 240°C. IR (neat): 2944s, 2859m, 1636w, 1451w, 1408w, 1329w, 1296w, 1273w, 1248w, 1192w, 1115w, 1078w, 1055m, 1030m, 986m, 939m, 918m, 835s, 797m, 766m, 745m, 731 m, 689m, 652m, 613s. ^{1}H-NMR (300 MHz): 5.92 (*dt*, *J*=4.5, 3.5, 1 Hz, 1H); 2.20-1.96 (*m*, 3H); 1.94-1.84 (*m*, 1H); 1.80-1.70 (*m*, 1H); 1.68-1.53 (*m*, 2H). ^{13}C-NMR (75.5 MHz): 126.1, 125.4, 35.3, 35.3, 35.2, 27.3, 20.6, -1.0. MS (70 eV): 234 (*M*+1, 4), 232 (M-1, 4), 80 (20), 79 (65), 74 (9), 73 (100), 45 (10). Anal. calc. for $C_9H_{17}BrSi$ (233.22): C 46.35, H 7.35, Br 34.26; found: C 46.52, H 7.46, Br 34.13

Preparation of 2-Bromo-3-trimethylsilylcyclopentene (2b). 2-Bromo-2-cyclopenten-1-one (14.19 g, 90 mmol) was dissolved in 225 ml of CH_3OH. After the addition of $CeCl_3 \cdot 7H_2O$ (33.52 g, 90 mmol), $NaBH_4$ (3.33 g, 90 mmol) was added slowly over 30 min. After an additional 5 min the ketone was consumed and the reaction was neutralized with 1 N HCl. The reaction mixture was diluted with H_2O (1 l) and extracted with Et_2O (3 x 500 ml). The combined extracts were washed with H_2O (500 ml), brine (500 ml), dried ($MgSO_4$), filtered, concentrated and distilled to give 2-bromo-2-cyclopenten-1-ol, 4. Yield 10.80 g (73%). B.p. 100°C/4 Torr.

To a soln. of 4 in 61 ml of THF at -78°C under argon was added methyllithium (29.3 ml of a 1.3 M soln. in Et_2O, 33.7 mmol). The reaction mixture was stirred for 5 min, and methanesulfonyl chloride (3.86 g, 33.7 mmol) was added *via* syringe. The reaction mixture was stirred 40 min at -78°C, and then transferred *via* syringe to a stirred soln. of trimethylsilylcopper. The soln. of trimethylsilylcopper was prepared as follows: To a soln. of hexamethyldisilane (11.24 g, 76.75 mmol) in HMPA (61 ml) at 8°C under argon was added methyllithium (66.7 ml of a 1.3 M soln. in Et_2O, 76.75 mmol) dropwise as the reaction mixture was chilled between -30°C to -40°C. After being stirred for 3 min, the resulting red solution was treated rapidly with copper (I) iodide (14.61 g, 76.75 mmol) in dimethyl sulfide (30 ml), which caused the reaction mixture to rise rapidly in temperature. The resulting black soln. was cooled to -20°C and stirred for 3 min. Et_2O (175 ml) was added and the reaction mixture was cooled to -60°C and stirred for 5 min. The reaction mixture was stirred for 1 h at -60°C to -50°C. It was then partitioned between 250 ml of petroleum ether and 250 ml of sat. NH_4Cl soln. buffered to pH 8 by addition of NH_4OH. The aq. phase was extracted with two 250-ml portions of pentane, and the combined org. extracts were washed with H_2O, brine, and dried over magnesium sulfate, filtered, and concentrated. The crude product 2b was chromatographed (hexane) and distilled. Yield 3.24 g (48%). B.p. 90°C/11 Torr. R_f=0.55 (hexane). GC: t_R=5.13

min., COV-17; program: 100°C (3 min), 20°C min, 260°C. IR (neat): 2953s, 2849m, 1607w, 1250s, 1181w, 1117w, 1040m, 949w, 866s, 837s, 787m, 752w, 693m. ^{1}H-NMR (300 MHz): 5.72 (br. *s*, 1H); 2.38-2.07 (*m*, 4H); 1.99-1.87 (*m*, 1H); 0.09 (*s*, 9H). ^{13}C-NMR (75.5 MHz): 128.2, 123.7, 40.1, 32.1, 26.9, -2.3.MS (70 eV): 219 (M^+, 24), 217 (21), 153 (24), 139 (59), 137 (57), 75 (21), 74 (15), 73 (100), 65 (12), 45 (21), 43 (17), 32 (14). Anal. calc. for $C_8H_{15}BrSi$ (219.20): C 43.84, H 6.90, Br 36.45; found: C 44.11, H 6.97, Br 36.63.

Preparation of Divinyl Alcohols 5, from Enals. General procedure. - A soln. of the appropriate vinyl bromide **2a** or **2b** (1.0 equiv) in dry THF (10 ml/mmol enal) in a 3-necked flask fitted with argon inlet, septum and thermometer was cooled to -78°C. *t*-Butyllithium (2.0 equiv) in pentane was added dropwise at -78°C until the vinyl bromide was consumed as indicated by GC analysis. A soln. of the appropriate enal 2 (1.0 equiv) in dry THF (1 ml/mmol enal) was added dropwise, as the temperature was maintained near -78°C. After complete addition, the reaction mixture was stirred for 1.5 h at -78°C. The flask was warmed to 0°C and the reaction was quenched with 4% NH_4Cl (10 ml/mmol enal). The mixture was extracted with Et_2O (3 x 10 ml/mmol enal), and the combined extracts were washed with equal volumes of H_2O and brine. The Et_2O extract was dried ($MgSO_4$) and concentrated to afford a crude product which was purified by chromatography (hexane/EtOAc 19:1) on silica gel and distillation.

(1-Cyclohexenyl)(6-trimethylsilyl-1-cyclohexenyl)methanol (**5aa**).Yield 70%. B.p. 125°C at 0.05 Torr. R_f=0.21 and 0.32 (hexane/EtOAc 19:1). GC: t_R = 11.15 and 11.27 min, COV-17; program: 110°C (3 min), 20°C/min, 260°C. IR (neat): 3376m, 2928s. 2857s, 1447m, 1437m, 1406w, 1339w, 1289m, 1246s, 1194w, 1171 w, 1138m, 1113w, 1086w, 1061w, 1044w, 1030 m, 1011 m, 970 w, 924 m, 833 s, 768 m, 750 m, 714 m, 685 m. ^{1}H-NMR (300 MHz): 5.77-5.63 (m, 1.82H); 5.50 (br. *t*, *J*=3.0 Hz, 0.18H); 4.31 (br. *s*, 0.65H); 4.29 (br. *s*, 0.35H); 2.14-1.88 (*m*, 5H), 1.88-1.68 (*m*, 3H); 1.68-1.34 (*m*, 8H); 0.05 (*s*, 3.15H); 0.04 (s, 5.85H). ^{13}C-NMR (75.5 MHz): 141.2, 140.4, 138.7, 138.2, 125.8, 122.3, 121.5, 116.9, 78.8, 78.6, 26.4, 26.2, 25.8, 25.7, 25.3, 25.2, 24.8, 24.3, 23.0, 22.7, 22.5, 21.2, 21.1, -0.42. MS (70 eV): 174 (43), 173 (29), 159 (10), 146 (61), 145 (69), 133 (17), 132 (63), 131 (100), 119 (10), 118 (34), 117 (52), 105 (20), 93 (10), 92 (11), 91 (45), 81 (20), 79 (33), 77 (17), 75 (48), 73 (97), 67 (20), 59 (12), 55 (13), 53 (13), 45 (35), 43 (17), 41 (28). Anal. calc. for $C_{16}H_{28}OSi$ (264.48): C 72.66, H 10.67; found: C 72.36; H 10.46.

(1-Cyclopentyl)(6-rimethylsilyl-1-cyclohexen-yl)methanol (**5ab**). Yield 72%. B.p. 115°C/0.05 Torr. R_f=0.20 and 0.27 (hexane/EtOAc 19:1). GC: t_R = 10.43 and 10.53 min, COV-17; program: 110°C (3 min) 20°C/min., 260°C. IR (neat): 3378w, 2942s, 2849s, 1453w, 1293w, 1248s, 1119w, 1134w, 1113w, 1086w, 1040w, 1030m, 1005w, 949w, 924w, 835s, 766w, 750w, 723w, 685m. ^{1}H-NMR (300 MHz): 5.72 (*m*, 0.63H); 5.67 (*m*, 0.37); 5.61 (*m*, 0.63H), 5.50 (*m*, 0.37H), 4.60 (br. *s*, 0.63H), 4.52 (br. *s*, 0.37H); 2.44-1.98 (*m*, 6H); 1.98-1.73 (*m*, 4H); 1.73-1.38 (*m*, 4H); 0.06 (*s*, 9H).^{13}C-NMR (75.5 MHz): 145.9, 145.6, 141.1, 141.0, 127.8, 125.2, 122.3, 117.0, 75.7, 73.1, 33.3, 32.3, 32.2, 30.4, 26.9, 26.0, 25.7, 25.3, 24.8, 24.4, 23.6, 23.2, 21.2, 21.1, -0.45. MS (70 eV): 160 (35), 159 (25), 158 (20), 145 (12), 132 (61), 131 (89), 129 (10), 119 (15), 118 (16), 117 (81), 104 (17), 91 (40), 79 (19), 77 (13), 75 (38), 73 (100), 67 (22), 59 (11), 45 (30), 43 (10), 41 (18).`Anal. calc. for $C_{15}H_{26}OSi$ (250.46): C 71.94, H 10.46; found: C 72.36, H 10.61.

(1-Cyclohexenyl)(5-trimethylsilyl-1-cyclopenten-yl)methanol (**5ba**). Yield 77%. B.p. 125°C/0.07 Torr. R_f=0.16 and 0.22 (hexane/EtOAc 9:1). GC: t_R = 8.69 and 8.84 min, COV-17; program: 140°C (3 min) 20°C/min, 280°C. IR (neat): 3364m, 3054w, 2930s, 2857m, 1437w, 1248s, 1016w, 953w, 835s, 752w, 733w, 693w. ^{1}H-NMR (300 MHz): 5.73 (*m*, 0.37H); 5.68 (*m*, 0.63H); 5.61 (*m*, 0.63H); 5.41 (br. *s*, 0.37H); 4.52 (br. *s*, 0.63H); 4.48 (br. *s*, 0.37H); 2.40-2.20 (*m*, 2H); 2.20-1.78 (*m*, 7H); 1.78-1.43 (*m*, 5H); 0.04 (*s*, 3.33H); 0.02 (s, 5.67H). ^{13}C-NMR (75.5 MHz): 148.0, 147.8, 138.8, 138.3, 125.7, 125.1, 122.1, 121.1, 76.5, 75.5, 34.9, 34.4, 32.1, 32.0, 27.9, 27.5, 25.5, 25.2, 24.9,

23.0, 22.7, 22.6, 22.5, -1.7, -1.6. MS (70 eV): 250 (m^+, 0.5), 160 (53), 159 (34), 158 (14), 145 (23), 132 (40), 131 (96), 119 (21), 118 (49), 117 (79), 105 (12), 104 (13), 92 (11), 91 (36), 81 (14), 79 (19), 77 (12), 75 (43), 73 (100), 67 (20), 59 (10), 45 (28), 41 (17). Anal. calc for $C_{15}H_{26}OSi$ (250.46): C 71.94, H 10.46; found: C 72.24, H 10.44.

(1-Cyclopentenyl)(5-trimethylsilyl-1-cyclopentenyl)methanol (5bb). Yield 78%. B.p. 105°C/0.07 Torr. R_f=0.18 and 0.22 (hexane/EtOAc 9:1). GC: t_R = 9.56 min, COV-17; program: 110°C (3 min), 20°C/min, 260°C. IR (neat): 3370m, 3050w, 2953s, 2849s, 1450w, 1406w, 1248s, 1186w, 1115w, 1042w, 1028w, 1013w, 953m, 835s, 733m, 714w, 689w, 652m. ^{1}H-NMR (300 MHz): 4.76 (*m*, 0.63H); 5.60 (m, 1H); 5.41 (bs, 0.37H); 4.80 (br. *s*, 0.67H); 4.73 (br. *s*, 0.37H); 2.50-2.00 (*m*, 7H); 2.00-1.77 (*m*, 2H); 1.69 (br. *s*, 0.37H); 1.73 (br. *s*, 0.63H); 0.02 (*s*, 3.33H); 0.01 (*s*, 5.67H). ^{13}C-NMR (75.5 MHz): 148.3, 147.5, 145.9, 127.8, 125.3, 125.2, 120.9, 70.5, 70.2, 35.0, 34.2, 32.7, 32.2, 32.0, 30.4, 27.7, 27.4, 23.5, 23.2, -1.8. MS (70 eV): 147 (13), 146 (94), 145(45), 131 (73), 119 (12), 118 (77), 117 (100), 105 (37), 104 (17), 97 (10), 92 (11), 91 (30), 81 (13), 80 (19), 79 (22), 77 (13), 75 (62), 73 (96), 67 (34), 45 (33), 41 (21), 32 (10). Anal. calc. for $C_{14}H_{24}OSi$ (236.48): C 71.12, H 10.23; found: C 71.03, H 10.18.

(2-Methyl-1-cyclopentenyl)(5-trimethylsilyl-1-cyclopentenyl)methanol (5bc). Yield 82%. B.p. 75°C/0.03 Torr. R_f=0.16 and 0.25 (hexane/EtOAc 9:1). GC: t_R = 9.86 and 9.97 min, COV-17 Program: 140°C (3 min), 10°C min, 280°C. IR (neat): 3345m, 3054w, 2952s, 2847s, 1445m, 1406w, 1381w, 1293w, 1248s, 1188w, 1115w, 1055w, 1015w, 977m, 953m, 901w, 835s, 752m, 691m. ^{1}H-NMR (300 MHz): 5.62 (*m*, 0.62); 5.25 (*m*, 0.38H); 4.98 (br. *s*, 1H); 2.45-1.40 (*m*, 12H); 1.73 (s, 3H); 0.06 (*s*, 3.42H); 0.03 (*s*, 5.58H). ^{13}C-NMR: (75.5 MHz): 148.9, 146.8, 136.5, 136.0, 135.3, 134.5, 123.9, 120.2, 68.1, 67.7, 39.0, 38.8, 34.9, 34.1, 32.1, 31.8, 30.9, 28.3, 27.3, 21.9, 21.5, 14.3, 14.0, -1.7, -1.8. MS (70 eV): 250 (M^+, 6), 232 (28), 161 (16), 160 (100), 159 (53), 158 (50), 146 (14), 145 (100), 143 (12), 133 (11), 132 (79), 131 (100), 130 (10), 119 (15), 118 (28), 117 (99), 105 (18), 104 (10), 95 (14), 91 (19), 81 (15), 80 (13), 79 (13), 75 (46), 73 (100), 67 (15). Anal. calc. for $C_{15}H_{26}OSi$ (250.46): C 71.93, H 10.46; found: C71.60 H10.57

(3-Methyl-1-cyclopentenyl)(5-trimethylsilyl-1-cyclopentenyl)methanol (5bd). Yield 75%. B.p. 130°C/0.4 Torr. GC: t_R = 9.72 and 9.93 min, COV-17; program: 140°C (3 min), 20°C/min, 280°C. IR (neat): 3362w, 3046w, 2952s, 2849m, 2361w, 1454w, 1404w, 1372w, 1248s, 1119w, 1076w, 1019w, 953w, 911w, 835s, 733w, 689w. ^{1}H-NMR (300 MHz): 5.42-5.61 (m, 3H), 4.78 (bs, 1H), 4.71-4.72 (m, 1H), 4.17 (bs, 1H), 2.86-2.68 (m, 2H), 2.41-1.30 (m, 18H), 1.05-0.92 (m, 8H), 0.04 (s, 9H), 0.02 (s, 9H).

Preparation of Divinyl Ketones 1. General procedure. - A stirred soln. of the divinyl alcohol (5) in dry CH_2Cl_2 (0.08 M)was cooled to 0°C and treated with 5 equiv of $BaMnO_4$. The mixture was warmed to r.t. and the progress of the reaction was monitored by T.L.C. Upon completion (24-48 h), the mixture was filtered through *Celite* and the solids were washed with CH_2Cl_2. The filtrate was concentrated, chromatographed (hexane/EtOAc 19:1) and distilled.

(1-Cyclohexenyl)(6-trimethylsilyl-1-cyclohexenyl) Ketone (1aa). Yield 71%. B.p. 180°C/0.25 Torr. R_f=0.62 (hexane/EtOAc 19:1). GC: t_R = 11.43 min, COV-17; program: 110°C (3 min), 20°C/min, 260°C. IR (neat): 2934s, 2859m, 1634s, 1449w, 1435w, 1375w, 1269m, 1246s, 1231s, 1194w, 1082w, 1026w, 980w, 930w, 879w, 835s, 733m, 770w, 689m, 664w. ^{1}H-NMR (300 MHz): 6.46-6.51 (*m*, 1H); 6.26 (*dt*, *J*=3.6, 1.5 Hz, 1H); 2.54-2.40 (*m*, 1H); 2.40-2.33 (*m*, 1H); 2.25-2.10 (*m*, 4H); 1.86-1.52 (*m*, 8H). ^{13}C-NMR (75.5 MHz): 199.7, 141.2, 139.1, 138.4, 135.7, 25.7, 25.4, 24.4, 24.3, 23.9, 22.1, 21.7, 20.7, -1.3. MS (70 eV): 262 (M^+, 30), 261 (15) 247 (14), 234 (12), 233 (34), 221 (11), 220 (22), 219 (27), 205 (15), 129 (12), 91 (11), 79 (12), 73 (100), 45 (23). Anal. calc. for $C_{16}H_{26}OSi$ (262.47): C 73.22, H 9.98; found: C 73.50, H 10.10.

(1-Cyclopentenyl)(6-trimethylsilyl-1-cyclohexenyl) Ketone (**1ab**). Yield 88%. B.p. 110°C/0.07 Torr. R_f=0.60 (hexane/EtOAc 19:1). GC: t_R = 10.68 min., COV-17; program: 110°°C (3 min), 20°C/min, 260°C. IR (neat): 2944s, 2855m, 1630s, 1456w, 1368w, 1294w, 1248s, 1192w, 1127w, 1084w, 1028w, 974w, 953w, 934w, 897w, 835s, 766w, 731m, 689w. ^{1}H NMR (300 MHz): 6.36-6.43 (*m*, 2H); 2.76-2.61 (*m*, 1H); 2.58-2.34 (*m*, 4H); 2.24-2.10 (*m*, 2H); 2.01-1.76 (*m*, 3H); 1.76-1.52 (*m*, 3H). -0.06 (s, 9H). ^{13}C-NMR: (75.5 MHz): 195.9, 144.9, 142.7, 142.4, 135.6, 33.8, 31.9, 25.4, 24.0, 23.9, 22.7, 20.7, -1.3. MS (70 eV): 248 (M^+, 14), 247 (15), 233 (18), 220 (38), 219 (32), 205 (27), 192 (13), 191 (16), 177 (12), 131 (10), 91 (12), 75 (45), 73 (100), 67 (10), 45 (29), 43 (19), 41 (14). Anal. calc. for $C_{15}H_{24}OSi$ (248.44): C 75.52, H 9.74; found: C 72.54, H 9.61.

(1-Cyclohexenyl)(5-trimethylsilyl-1-cyclopentenyl) Ketone (**1ba**). Yield 70%. M.p. 51.5 -53°C (pentane). R_f=0.58 (hexane/EtOAc 19:1). GC: t_R = 8.90 min.,COV-17; program: 140°C (3 min), 20°C/min, 280°C. IR (melt): 2936s, 1632s, 1599m, 1449w, 1435w, 1375w, 1345w, 1306w, 1283w, 1248s, 1200w, 1177m, 1100w, 972w, 955w, 928w, 914w, 837s, 793w, 752w, 737m, 696m. ^{1}H-NMR (300 MHz): 6.64-6.58 (*m*, 1H); 6.15 (*d*, *J*=2.1 Hz, 1H); 2.56 -2.38 (*m*, 4H); 2.30-1.78 (*m*, 5H); 1.72-1.55 (*m*, 4H); -0.06 (*s*, 9H). ^{13}C-NMR (75.5 MHz): 195.9, 146.7, 139.5, 139.1, 33.7, 33.6, 26.5, 25.8, 23.8, 22.0, 21.7, -2.2. MS (70 eV): 248 (M^+, 21), 233 (19), 220 (22), 219 (24), 206 (10), 205 (24), 75 (35), 73 (100), 45 (23). Anal. calc. for $C_{15}H_{24}OSi$ (248.44): C 72.51, H 9.74; found: C 72.54, H 9.70.

(1-Cyclopentenyl)(5-trimethylsilyl-1-cyclopentenyl) Ketone (**1bb**). Yield 80%. M.p.: 42 - 42.5°C (pentane). R_f=0.52 (hexane/EtOAc 19:1). GC: t_R = 10.02 min., COV-17; program: 140°C (3 min), 10°C/min, 260°C. IR (melt): 3061w, 2953s, 1630s, 1437w, 1366m, 1300w, 1248s, 1192w, 1171m, 1109w, 957m, 930w, 837s, 762m, 729m, 693w. ^{1}H-NMR (300 MHz): 6.50 (*m*, 1H); 6.32 (*d*, *J*=1.7 Hz, 1H); 2.76-2.58 (*m*, 1H); 2.58-2.41 (*m*, 6H); 2.23-2.07 (*m*, 1H); 2.03-1.80 (*m*, 3H). ^{13}C-NMR (75.7 MHz): 191.9, 147.9, 145.4, 142.9, 139.1, 33.8, 33.7, 33.3, 31.6, 26.6, 22.7, -2.2. MS (70 eV): 234 (M^+, 14), 219 (22), 206 (30), 205 (13), 191 (24), 178 (11), 117 (10), 75 (47), 73 (100), 67 (10), 65 (12), 45 (23). Anal. calc. for $C_{14}H_{22}OSi$ (234.41): C 71.73, H 9.46; found: C 71.51, H 9.48.

(2-Methyl-1-cyclopenten-1-yl)(5-trimethylsilyl-1-cyclopentenyl) Ketone (**1bc**). Yield 80%. M.p. 32 - 32.5°C (pentane). R_f=0.41 (hexane/EtOAc 19:1). GC: t_R = 10.33 min., COV-17; program: 140°C (3 min), 10°C/min, 280°C. IR (melt): 3056w, 2952s, 1626s, 1601s, 1437m, 1364m, 1298w, 1283w, 1248s, 1175m, 1111w, 1013w, 955m, 899w. ^{1}H-NMR (300 MHz): 6.4 (*m*, 1H); 2.85-2.65 (*m*, 2H); 2.65-2.34 (*m*, 5H); 2.25-2.05 (*m*, 2H); 2.05-1.60 (*m*, 5H); -0.02 (*s*, 9H). ^{13}C-NMR (75.7 HMz): 194.6, 148.9, 146.1, 142.0, 136.8, 39.9, 35.9, 33.8, 32.4, 26.9, 22.2, 16.3, -2.0. MS (70 eV): 207 (17), 206 (22), 205 (100), 203 (14), 192 (24), 191 (18), 177 (11), 159 (19), 131 (13), 75 (39),73 (69). Anal. calc. for $C_{15}H_{24}OSi$ (248.44): C 72.52, H 9.74; found: C 72.44, H 9.67.

(3-Methyl-1-cyclopentenyl)(5-trimethylsilyl-1-cyclopentenyl) Ketone (**1bd**). Yield 78%. B.p.: 105°C/0.3 Torr. GC: t_R = 10.21, COV-17, 140°C (3 min), 10°C/min, 280°C. IR (neat): 3052w, 2955s, 2870m, 1630s, 1364w, 1248s, 1173m, 1113w, 1080w, 959w, 930w, 839s, 760m, 731m. ^{1}H-NMR (300 MHz): 6.32-6.37 (*m*, 2H); 3.03-2.40 (*m*, 6H); 2.22-2.09 (m, 2H), 1.99-1.89 (m, 1H), 1.52-1.38 (*m*, 1H); 1.12 (*d*, *J*=7, 1.5 H); 1.07 (*d*, *J*=7, 1.5 H); -0.38 (*s*, 4.5 H); -0.03 (*s*, 4.5H). ^{13}C-NMR: (75.5 MHz): 192.2, 192.1, 148.0, 147.9, 144.2, 143.9, 139.3 139.0, 41.3, 41.1, 33.7, 33.5, 33.3, 31.7, 31.5, 31.4, 31.0, 26.7, 20.1, 19.8, -2.1.

Cyclization of 1aa. - A stirred mixture of anhydrous $FeCl_3$ (170 mg, 1.05 mmol) and 40 ml of dry CH_2Cl_2 (0.02 M) under argon was cooled to -50°C. To the greenish-yellow heterogenous mixture was added dropwise a soln. of the *divinyl ketone* **1aa** *(262 mg, 1 mmol) in 10 ml of* CH_2Cl_2. The reddish-brown mixture was allowed to stir 1 min and then quenched by the addition of brine (50 ml) and diluted with Et_2O (50 ml). The H_2O layer was separated, extracted with Et_2O (2 x 50 ml) and the combined Et_2O extracts were washed with H_2O (75 ml), brine (75 ml), and then dried ($MgSO_4$) and

evaporated to afford a clear and colorless oil. GC-MS: column; COV-17 program: (140°C(3 min), 10°C/min, 260°C) t_R = 10.15 min (A, 89.0%), M^+ 190; t_R = 10.45 min (B, 6.7%), M^+ 190; t_R = 10.61 min (C, 2.7%), M^+ 190; t_R = 11.58 min (D, 0.9%), M^+ 188; t_R = 12.13 min (E, 0.6%), M^+ 224.

(4ab,4ba,9aa)-1,2,3,4,4a,4b,5,6,7,9a-decahydro-1H-fluoren-9-one ((*t,a*)-**6aa**). Yield 157 mg (79%) after distillation and recrystallization. B.p. 85°C/0.3 Torr; m.p. 78.5 - 79.5°C (pentane). *Rf*: 0.23 (hexane/EtOAc 19:1). GC: t_R = 10.14 min, COV-17; program: 140°C (3 min), 10°C/min, 260°C. IR (neat): 2921s, 2854s, 2813w, 1713s, 1653s, 1449s, 1415m, 1363w, 1349w, 1293m, 1244m, 1232w, 1222 w, 1208m, 1196w, 1173w, 1144w, 1096m, 1072w, 935m. ^{1}H-NMR (300 MHz): 6.64 (*d*, *J*=2.6, 1H), 2.35-2.19 (*m*, 1H), 2.19-1.61 (*m*, 6H), 1.70-1.91 (*m*, 3H), 1.55-1.37 (*m*, 1H), 1.30-0.84 (*m*, 6H). ^{13}C-NMR (75.5 MHz): 204.7, 141.0, 131.5, 54.9, 48.1, 42.4, 30.3, 26.5, 25.9, 25.5, 25.1, 21.4. MS (70 eV): 190 (M^+, 82), 163 (11), 162 (84), 161 (32), 149 (10), 148 (14), 147 (18), 134 (11), 133 (19), 109 (15), 108 (100), 98 (20), 94 (50), 81 (24), 80 (55), 79 (39). Anal. calc. for $C_{13}H_{18}O$ (190.29): C 82.06, H 9.53; found: C 82.11, H 9.54.

Base-Catalyzed Epimerization of (*t,a*)-6aa. - The enone (*t,a*)-**6aa** (100 mg, 0.53 mmol) was placed in 10 ml of freshly distilled methanol. Sodium methoxide (0.05 equiv of a 0.45 M solution in methanol) was added and the soln. was stirred at r.t. The equilibration was monitored by capillary GC until the ratios of products were constant. After 12 h the reaction mixture was poured onto 100 ml of H_2O and extracted with Et_2O (3 x 50 ml). The Et_2O extracts were washed with H_2O (50 ml) and brine (50 ml), dried ($MgSO_4$) and evaporated to yield 93 mg (93%) of a mixture of (*t,a*)-**6aa** and (*c,a*)-**6aa** which was separated on a chromatotron using petroleum Et_2O and EtOAc(30:1) to afford 50.7 mg of (*t,a*)-**6aa** (50.7 %) and 23.3 mg of (*c,a*)-**6aa** (23.3 %). *Rf*: (*t,a*)-**6aa**, 0.20; (*c,a*)-**6aa**, 0.17 (petroleum ether/EtOAc 30:1);

(4ab,4ba,9ab)-1,2,3,4,4a,5,6,7,9a-decahydro-1H-fluoren-9-one ((*c,a*)-**6aa**). B.p.: 140°C/0.1 Torr. *Rf*=0.17 (petroleum ether/EtOAc 30:1). IR (neat): 2926m, 2857m, 1719m, 1649m, 1449m, 1422w, 1246w, 1221m, 1179m, 1140w, 109w, 1067 w, 951w, 901w, 774w, 700m, 650m. ^{1}H-NMR (300 MHz): 7.26-6.70 (*m*, 1H); 2.65-2.53 (*m*, 1H); 2.40-2.06 (m, 4H); 1.95-1.67 (*m*, 5H); 1.64-1.45 (*m*, 3H); 1.43-1.15 (*m*, 3H); 0.98-0.85 (*m*, 1H). ^{13}C-NMR (300 MHz): 207.7, 141.0, 133.4, 48.4, 40.2, 37.0, 27.2, 25.7, 24.7, 24.0, 23.8, 21.7, 20.8.

Reaction of (*t,a*)-6aa with Thiosemicarbazide. To a soln. of the (*t,a*)-**6aa** (50 mg, 0.26 mmol) and thiosemicarbazide (1.48 g, 16.3 mmol) in 25 ml of EtOH/H_2O 3:1 was added 7 drops of glacial acetic acid as catalyst. After heating the soln. at 60°C for 36 h the solvent was removed *in vacuo*, and the remaining solid was dissolved in H_2O (25 ml) and Et_2O (25 ml). The H_2O was washed with Et_2O (2 x 25 ml) and the Et_2O extracts were washed with H_2O (25 ml) and brine (25 ml), dried ($MgSO_4$) and evaporated to afford after chromatography on silica gel (hexane/EtOAc,4:1) 32.4 mg (47%) of the thiosemicarbazone, which was recrstallized from CH_2Cl_2/petroleum ether. ^{1}H NMR analysis showed 10% of the *cis*-thiosemicarbazone was present, which was a result of epimerization. M.p. 169°C, 50% dec. and 197°C, 50% dec. ^{1}H-NMR (300 MHz): 6.62 (br. *s*, 1H, H-C(8)). ^{13}C-NMR: (75.5 MHz): 179.4 C(9).

Reaction of (*c,a*)-6aa with Thiosemicarbazide. - To a soln. of (*c,a*)-**6aa** (18 mg, 0.09 mmol) and thiosemicarbazide (541 mg, 16.3 mmol) in 10 ml of EtOH/H_2O 3:1 was added 3 drops of glacial acetic acid as catalyst. After heating the soln. at 60°C for 3 days, the solvent was removed under reduced pressure, and the remaining solid was dissolved in H_2O (10 ml) and Et_2O (10 ml). The H_2O was washed with Et_2O (2 x 10 ml) and the Et_2O extracts were washed with H_2O (10 ml) and brine (10 ml), dried ($MgSO_4$) and evaporated to afford after chromatography on silica (hexane/EtOAc 4:1) and recrystallization from ethyl acetate 13.1 mg (55%) of the thiosemicarbazone as a white solid. ^{1}H-NMR analysis showed less than 5% of the *trans*-thiosemicarbazone was present as a result of epimerization. M.p.: 199.5-

200.5°C dec. ^{1}H-NMR (300 MHz): 6.46 (*d*, 1H, H-C(8)). ^{13}C-NMR (75.5 MHz): 178.4 C(9), 158.8, 138.7, 125.2, 42.1, 39.5, 38.3, 27.2, 25.6, 24.6, 23.9, 23.5, 21.9, 20.6.

Cyclization of 1ab. - A stirred mixture of anhydrous $FeCl_3$ (170 mg, 1.05 mmol) and 40 ml of dry CH_2Cl_2 (0.02 M) under argon was cooled to -50°C. To the greenish-yellow heterogenous mixture was added dropwise a soln. of **1ab** (248 mg, 1 mmol) in 10 ml of CH_2Cl_2. The resulting reddish-brown mixture was allowed to stir for 15 min and then quenched by the addition of brine (50 ml) and diluted with Et_2O (50 ml). The H_2O layer was separated, extracted with Et_2O (2 x 50 ml) and the combined Et_2O extracts were washed with H_2O (50 ml), brine (50 ml), and then dried ($MgSO_4$) and evaporated to afford **6ab** as a yellow oil.

(3ab,3ba,8ab)-2,3,3a,3b,4,5,6,8a-Octahydro-1H-cyclopent[a]inden-8-one ((*t,a*)-**1ab**). Yield 155 mg (88%) after column chromatography (hexane/EtOAc 19:1) and distillation. B.p. 100°C/0.35 Torr. R_f=0.20 (hexane/EtOAc 19:1). GC: t_R = 9.08 min, COV-17; program: 140°C (3 min), 10°C/(min), 260°C. IR: (neat): 2928s, 2861m, 1713s, 1651s, 1449w, 1422w, 1260w, 1223m, 1188w, 1129w, 1080w, 988w, 943w, 893w, 820w, 770w, 683w. ^{1}H-NMR (300 MHz): 6.50 (*m*, 1H); 2.63 (*ddt*, *J*=10.2, 5.0, 1.4 Hz, 1H); 2.32-1.99 (*m*, 5H); 1.97-1.37 (*m*, 8H); 1.15-0.85 (*m*, 1H). ^{13}C-NMR (75.5 MHz): 209.6, 142.7, 131.6, 52.8, 46.5, 42.7, 32.0, 29.5, 28.3, 25.7, 25.2, 22.0. MS (70 eV): 176 (M^+,45), 149 (12), 148 (100), 147 (14), 133 (26), 120 (26), 119 (17), 108 (68), 107 (22), 106 (12), 105 (13), 92 (18), 91 (23), 81 (12), 80 (65), 79 (57), 78 (11), 64 (14). Anal. calc. for $C_{12}H_{16}O$ (176.26): C 82.06, H 9.53; found: C 82.11, H 9.54.

Cyclization of 1ba. - A stirred mixture of anhydrous $FeCl_3$ (170 mg, 1.05 mmol) and 40 ml of dry CH_2Cl_2 (0.02 M) under argon was cooled to -20°C. The a soln. of **1ba** (248 mg, 1 mmol) in 10 mL of CH_2Cl_2 was added dropwise to the greenish-yellow heterogenous mixture. The resulting reddish-brown mixture was allowed to stir for 45 min and then quenched by the addition of brine (50 ml) and diluted with Et_2O (50 ml). The H_2O layer was separated, extracted with Et_2O (2 x 50 ml) and the combined Et_2O extracts were washed with H_2O (50 ml), brine (50 ml), and then dried ($MgSO_4$) and evaporated to afford (*t,a*)-**6ba** yellow semi-crystalline product.

(3aa,3bb,7aa)-3,3a,3b,4,5,6,7,7a-Octahydro-2H-cyclopent[a]inden-8-one ((*t,a*)-**6ba**). Yield 63 mg (36%) after chromatography (hexane/EtOAc 19:1) and distillation. B.p. 90°C/0.3 Torr; m.p.: 59 - 63°C (pentane). R_f=0.17 (hexane/EtOAc 19:1). GC: t_R = 8.28 min COV-17; program: 140°C (3 min), 10°C/min, 260°C. IR (melt): 2924s, 2853m, 1717s, 1630m, 1447w, 1354w, 1231w, 1208w, 1179w, 1138w, 1100w, 1080w, 1030w, 951w, 758m. ^{1}H-NMR (300 MHz): 6.48 (*d*, *J*=2.6, 1H); 2.89-2.59 (*m*, 3H); 2.27 (*dt*, *J*=12.5, 7.1, 1H); 2.15-2.04 (*m*, 1H); 2.04-1.88 (*m*, 2H); 1.88-1.69 (*m*, 2H); 1.57 (*ddt*, *J*=10.3, 9.3, 1.9, 1H); 1.29-1.05 (*m*, 5H). ^{13}C-NMR (75.5 MHz): 201.9, 149.9, 133.7, 61.1, 52.3, 50.8, 37.6. 31.7. 30.7, 25.8, 25.6, 25.4. MS (70 eV): 176 (M^+, 33), 95 (11), 94(100), 66 (15). Anal. calc. for $C_{12}H_{16}O$ (176.26): C 81.77, H 9.15; found: C 81.76, H 9.20.

Base-Catalyzed Epimerization of (*t,a*)-6ba. - The enone (36.5 mg, 0.21 mmol) was dissolved on 3.5 ml of 2-propanol-d. 1,8-Diazabiclo[5.4.0]undec-7-ene (0.05 eq) was added and the soln. was stirred at r.t. The equilibration was monitored by capillary GC until the ratios of products was constant. After 12 h the reaction mixture was poured onto 15 ml of water and extracted with Et_2O (3 x 15 ml). The Et_2O extracts were washed with H_2O (15 ml) and brine (15 ml), dried ($MgSO_4$) and evaporated to yield 34.2 mg (92%) of a mixture of (*t,a*)-**6ba** (84.17 %) and (*c,a*)-**6ba** (15.83%). ^{1}H-NMR (300 MHz) showed complete exchange of hydrogen for deuterium. R_f= 0.16 ((*t,a*)-**6ba**) and 0.07 ((*c,a*)-**6ba**) (hexane/EtOAc 9:1). GC: t_R = 7.96 min. ((*t,a*)-**6ba**) and 8.26 min. ((*c,a*)-**6ba**), COV-17; program: 140°C (3 min), 10°C/min, 280°C.

Cyclization of 1bb. - To a 10°C soln. of the **1bb** (210 mg, 0.90 mmol) in 225 ml of dry CH_2Cl_2 (0.004 M) under argon was added dropwise BF_3-Et_2O (116 ml, 0.95 mmol). The resulting soln. was stirred for 10 min and then quenched by addition of 225 ml of 10% $NaHCO_3$. The H_2O layer was separated, extracted with CH_2Cl_2 (2 x 75 ml) and the combined CH_2Cl_2 extracts were washed with H_2O (200 ml), brine (200 ml) and then dried ($MgSO_4$) and evaporated to afford an oil which was purified by distillation.

(3aa,3bb,6ab)-2,3,3a,3b,4,5,6,6a-Octahydro-2H-cyclopenta[a]pentalen-7-one (**6bb**). Yield 112 mg (77%) after distillation. B.p. 90°C/0.3 Torr. R_f=0.27 (hexane/EtOAc 9:1). GC: t_R = 7.16 min, COV-17; program: 140°C (3 min), 10°C/min, 280°C. IR (neat): 3058w, 2952s, 2869m, 1711s, 1634m, 1451w, 1435w, 1318w, 1287w, 1258w, 1215m, 1181w, 1142w, 1057w, 968w, 951w, 801w. ^{1}H-NMR (300 MHz): 6.41 (*m*, 1H); 2.99-2.78 (*m*, 2H); 2.76-2.62 (*m*, 2H); 2.44-2.26 (*m*, 2H); 1.96-1.57 (*m*, 7H). ^{13}C-NMR (75.5 MHz): 205.3, 151.2, 133.5, 58.7, 53.0, 47.7, 37.7, 35.6, 32.4, 29.5, 26.1. MS (70 eV): 162 (M^+, 50), 134 (15), 95 (11), 94 (100), 93 (20), 92 (10), 91 (13), 67 (19), 66 (48). Anal. calc. for $C_{11}H_{14}O$ (162.23): C 81.44, H: 8.70; found: C 81.21, H 8.63.

Cyclization of 1bc. - To a 20°C soln. of **1bc** (174 mg, 0.70 mmol) in 175 ml of dry CH_2Cl_2 (0.004 M) under argon was added dropwise BF_3-Et_2O (90.4 ml, 0.74 mmol). The resulting soln. was stirred for 3.5 h and then quenched by addition of 175 ml of 10% $NaHCO_3$. The H_2O layer was separated, extracted with CH_2Cl_2 (2 x 50 ml) and the combined CH_2Cl_2 extracts were washed with H_2O (150 ml), brine (150 ml) and then dried ($MgSO_4$) and evaporated to afford an oil which was purified by chromatography and distillation.

(3aa,3bb,6ab)-2,3,3a,3b,4,5,6,6a-Octahydro-3b-methyl-2H-cyclopenta[a]pentalen-7-one (**6bc**). Yield 96.5 mg (78.5%) after chromatography (hexane/EtOAc 9:1) and distillation. B.p.: 50°C/0.10 Torr. R_f=0.31 (hexane/EtOAc 9:1). GC: t_R = 7.40 min, COV-17; program: 140°C (3 min), 10°C/min, 280°C. IR (neat): 3056w, 2957s, 2869s, 1711s, 1634s, 1449m, 1375m, 1312w, 1275m, 1221s, 1184m, 1132m, 1053m, 1015m, 984w, 963m, 899w, 820m, 783w, 731m. ^{1}H-NMR (300 MHz): 6.39 (*dt*, *J*=3.0, 2.9m Hz, 1H); 3.17-3.05 (*m*, 1H); 2.80-2.58 (*m*, 2H); 2.42 (*dd*, *J*=10.9, 5.9, 1H); 2.09-1.63 (*m*, 7H); 1.52-1.36 (*m*, 1H); 0.98 (*s*, 3H). ^{13}C-NMR (75.5 MHz): 204.9, 149.9, 133.6, 66.8, 54.8, 48.0, 40.3, 37.6, 29.9, 27.5, 26.0, 22.3. MS (70 eV): 176 (M^+,10), 148 (7), 95 (9), 94 (100), 66 (24). Anal. calc. for $C_{12}H_{16}O$ (176.26): C 81.77, H 9.15; found: C 81.61, H 9.27.

Cyclization of Divinyl Ketone 1bd. - To a cold (10°C) soln. of **1bd** (100 mg, 0.4 mmol) in 100 ml of CH_2Cl_2 (0.004 M) under argon was added dropwise BF_3-Et_2O (51.7 ml, 0.42 mmol). The resulting solution was stirred for 1 h and then quenched by addition of 100 ml of 10% $NaHCO_3$. The H_2O layer was separated, extracted with CH_2Cl_2 (2 x 50 ml) and the combined CH_2Cl_2 extracts were washed with H_2O (100 ml), brine (100 ml) and then dried ($MgSO_4$) and evaporated to afford an oil which was purified by chromatography and distillation.

(3aa,3bb,6ab)-2,3,3a,3b,4,5,6,6a-Octahydro-4-methyl-2H-cyclopenta[a]pentalen-7-one (**1bd**). Yield 58.3 mg (83%) after chromatogrnphy (hexane/EtOAc 9:1). B.p. 110°C/0.75 Torr. R_f=0.27 (hexane/EtOAc 9:1). IR (neat): 2953s, 2872m, 2361w, 1711s, 1634s, 1456m, 1435w, 1377w, 1285, 1258w, 1215m, 1181w, 1138w, 1057w, 1036w, 951w, 909w, 868w, 799w, 733w. ^{1}H-NMR (300 MHz): 6.40-6.48 (*m*, 1H), 2.83-3.09 (*m*, 2H), 2.61-2.80 (*m*, 2H), 2.45-1.58 (*m*, 7H), 1.42-1.30 (*m*, 1H), 1.03 (*d*, *J* = 7.7, 1.5 H), 0.93 (*d*, *J* = 7.0, 1.5H). ^{13}C-NMR (75.5 MHz): 205.6, 205.0, 151.3, 151.0, 133.4, 133.1, 58.5, 57.7, 55.7, 53.8, 53.3, 47.0, 40.7, 38.0, 37.9, 37.7, 36.0, 35.7, 34.3, 32.7, 28.8, 28.1, 20.7, 15.1.

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