19. Silicon-Directed *Nazarov* Cyclizations

Part V

Substituent and Heteroatom Effects on the Reaction

by **Scott E. Denmark***, **Karl L. Habermas**, and **Gary A. Hite**[1])

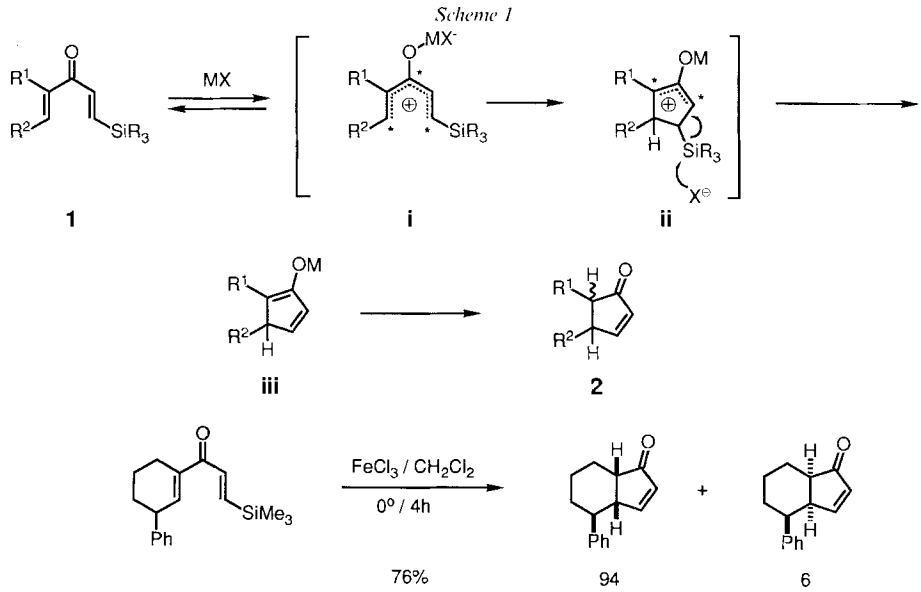
Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, IL 61801, USA

(13.VIII.87)

The ability to incorporate alkyl, alkenyl, aryl, and heteroatomic groups into substrates for the silicon-directed *Nazarov* cyclization and their subsequent reactions has been investigated. In general, most of the groups are compatible with the conditions for the cyclization and do not interfere even when directly attached to the divinyl ketone. The influence of substituents on the rate of the cyclization has been addressed and is consistent with a simple mechanistic picture. O- and N-Containing functions are tolerated except when attached to the α-vinyl C-atom of the divinyl ketone. The diastereoface-directing effect of a fused cyclobutane is discussed.

Introduction. – Previous publications from these laboratories [1] have demonstrated the utility of the silicon-directed *Nazarov* cyclization (SDNC) as a versatile method for cyclopentenone annellation *(Scheme 1)*. The reaction has been shown to proceed under

Scheme 1

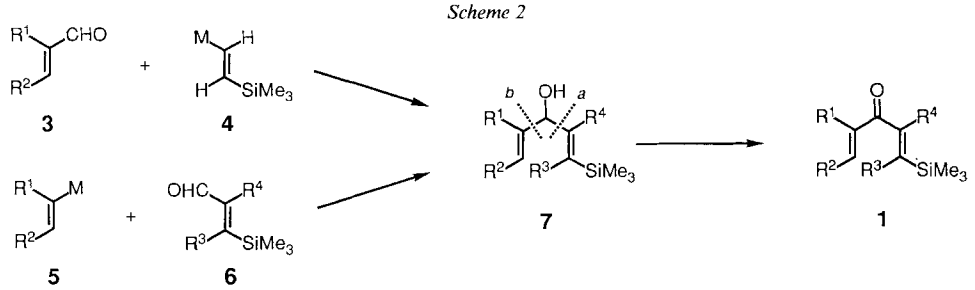


[1]) Taken in part from the M. S. Thesis of *G. A. H.*, University of Illinois, Urbana, IL, 1987.

mild conditions to afford, exclusively, the thermodynamically less stable cyclopentenone tautomer **2** as predicted by the silicon-directed cation collapse (see **ii**). The substrates **1** (prepared from readily available precursors [2]) can vary widely in structure in both cyclic and acyclic frameworks [1b]. We have investigated the degree of diastereoface selection in the annellation reaction with chiral substrates as a function of ring size [1d], ring-substituent position and size [1c] [1d], and silicon-group size [1d]. Good-to-excellent stereoselectivities have been obtained in cyclohexenyl systems; *Scheme 1* shows a typical example. The degree and direction of stereocontrol was found to be predictable using simple principles. Finally, mechanistic studies [1c] led us to propose that the rate-limiting step of the SDNC is a conrotatory cyclization of the initially formed pentadienyl cation **i** to the cyclopentenyl cation **ii**. This process is associated with a net transfer of positive charge for the positions labeled with asterisks in the two proposed intermediates **i** and **ii** in *Scheme 1*. The present study was undertaken to address two objectives: 1) to examine the effects on reaction rate of various substituents at the olefinic C-atoms of the divinyl ketone **1** and 2) to assess the compatibility of the reaction with diverse functional groups including olefins, ethers, esters, and carbamates.

Synthesis of β-Silyl-Substituted Divinyl Ketones 1. – Two general approaches to the construction of the precursors have been developed which are illustrated in *Scheme 2*. The formation of the divinylmethyl alcohols **7** and subsequent oxidation to the divinyl ketones **1** proceeded in good yields. The preparation of some of the less readily available starting materials **3**–**6** and comments on specific condensations are discussed below.

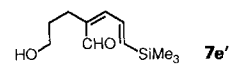
Scheme 2



1. *Enal* **3** *and (β-Silylvinyl)metal* **4**. – For the disconnection *a* in *Scheme 2*, we required access to α,β-unsaturated aldehydes **3** and the *Grignard* reagent from (*E*)-(2-bromoethenyl)trimethylsilane [3] (see *Table 1*). Of the enals employed, **3f** and **3g** are commercially available, while **3a**, **3c**, **3e**, and **3h** were prepared according to literature methods (see *Exper. Part*). The enals **3b** and **3d** were prepared by the usual sequence from **8** and **9**, respectively, as illustrated in *Scheme 3*. However, in these cases we found that $NaBH_4$/$CeCl_3$ [4] was necessary to suppress the undesirable conjugate reduction with $LiAlH_4$. With this reagent, **9** gave, in addition, the acetal **10** and the alcohol **11** which were converted to **3d** by hydrolysis and oxidation, respectively.

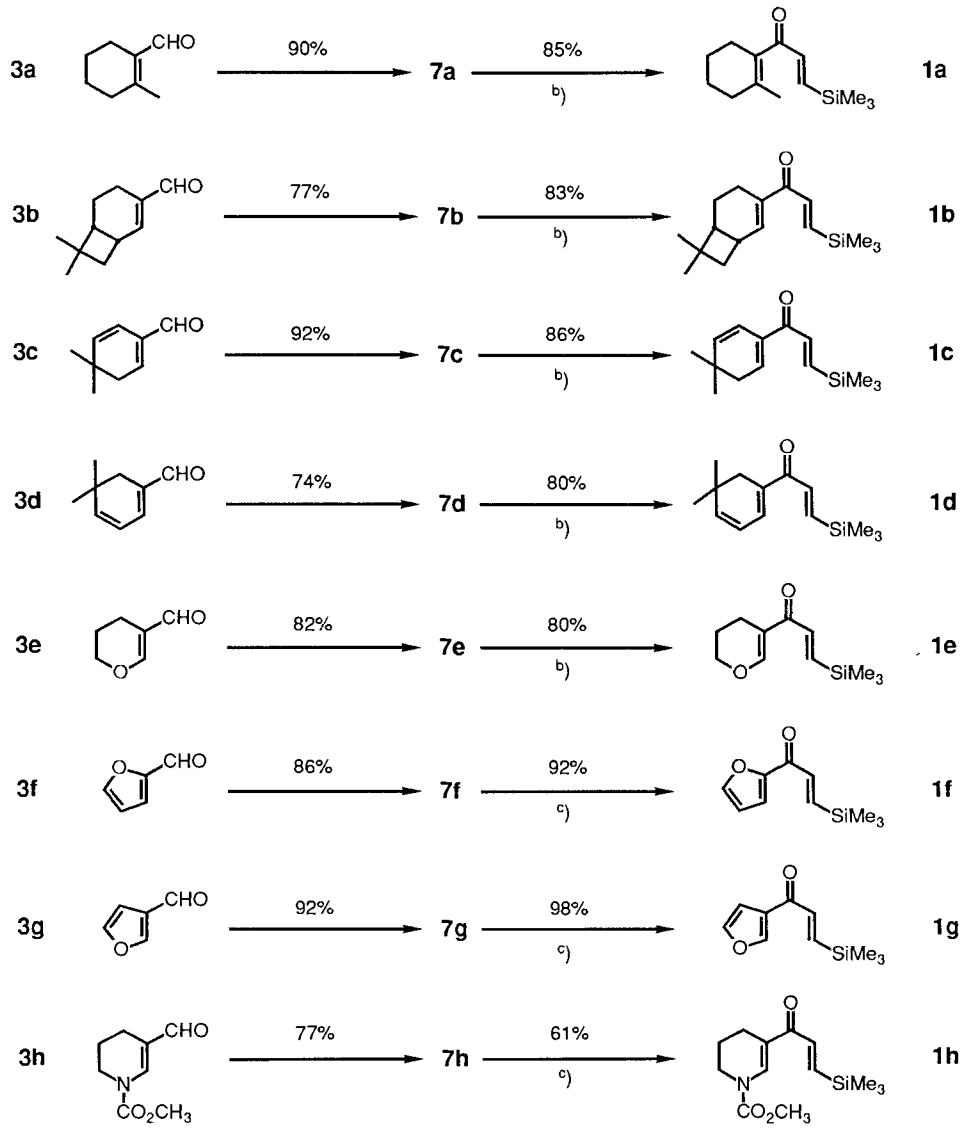
Additions of the (silylvinyl)magnesium reagent to **3** occurred in good yield (74–92%) to afford the divinylmethyl alcohols **7** which all (except **7e**[2])) could be purified by

[2]) Since **7e** is a vinylogous hemiacetal, it underwent rearrangement to **7e'** on silica gel.



7e'

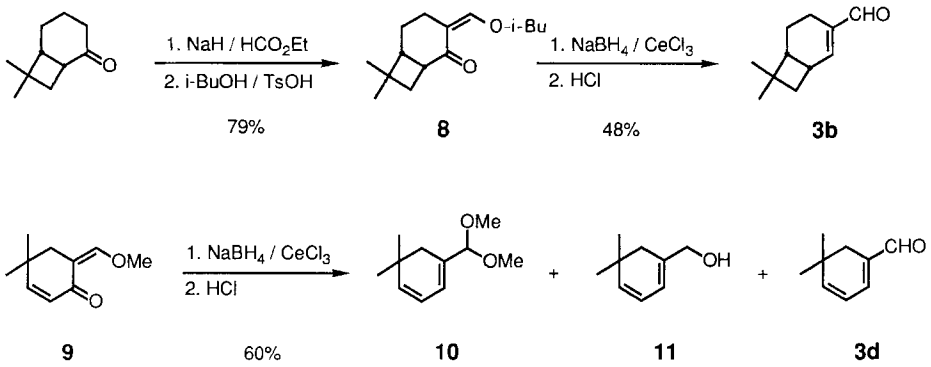
Table 1. *Divinyl Ketones* **1a–h** *from Enals* **3a–h**[a])



[a]) Yield after chromatography.
[b]) $BaMnO_4$.
[c]) NiO_2.

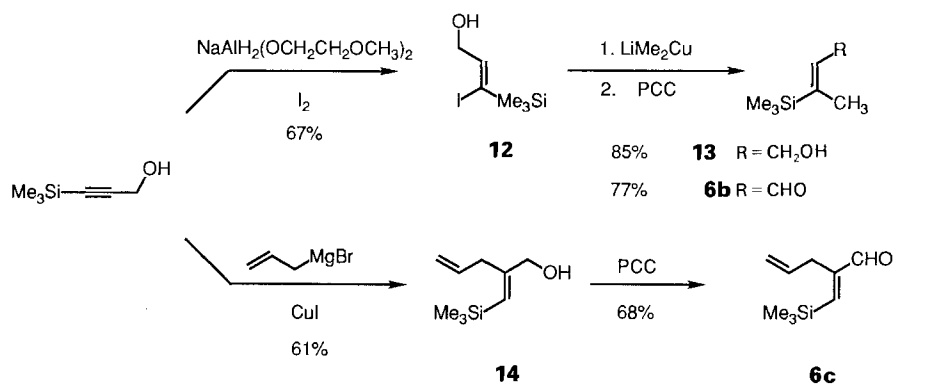
chromatography and distillation *(Table 1)*. The previously preferred oxidant NiO_2 gave good yields only for **1f–h**. For more sensitive substrates, freshly prepared $BaMnO_4$ [5] was employed (→**1a–e**).

Scheme 3



2. *β-Silylenals* **6** *and Vinylmetals* **5**. – For the disconnection *b* in *Scheme 2*, three different enals **6** were used of which **6a** ($R^3 = R^4 = H$, *Scheme 2*) has been previously described [2c]. The substituted β-silylenals **6b** and **6c** were both prepared from 3-(trimethylsilyl)-2-propynol [2a] as outlined in *Scheme 4*. The original *Stork* [6] procedure for the synthesis of **12** was modified, using sodium bis(2-methoxyethoxy)aluminum hydride in

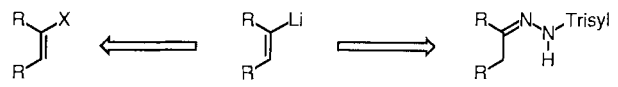
Scheme 4



the reduction and AcOEt before iodination to consume excess hydride. Oxidation of the intermediate alcohol **13** was performed with pyridinium chlorochromate (PCC) [7]. The β-silylenal **6c** was available from a regioselective allylcupration [8] (→**14**) followed by PCC oxidation.

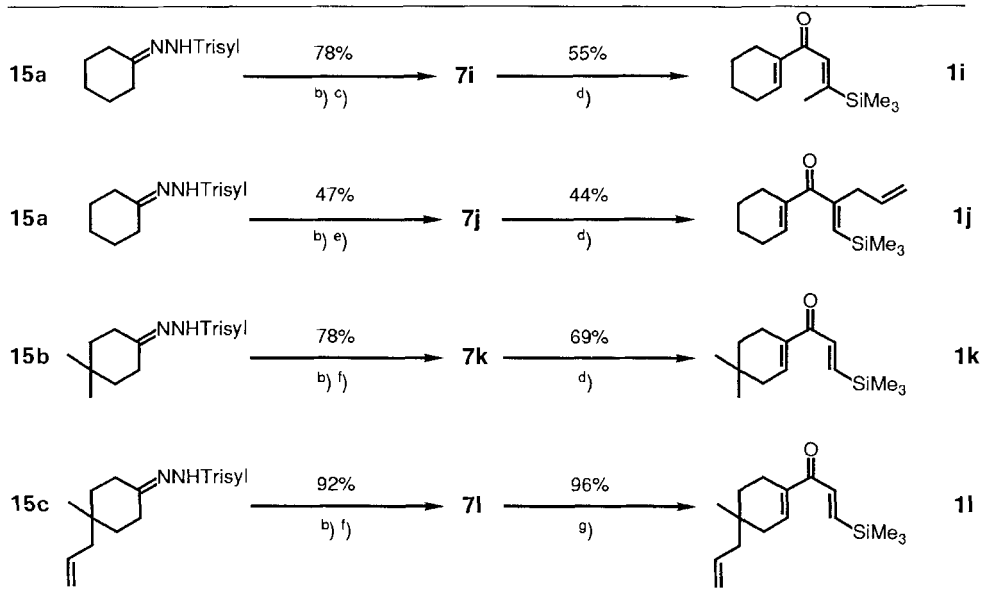
The vinyl organometallic reagents **5** were generated either by decomposition of trisylhydrazones **15** or by Br/Li exchange or direct deprotonation from **16** as shown in *Scheme 5*. We have previously described the utility of the *Bond-Shapiro* [9] route to **5** starting from **15**. The yields for the subsequent addition to **6a–c** and oxidation of the divinylmethyl alcohols to **1i–l** are collected in *Table 2*. The ketone precursor **19** to hydrazone **15c** was prepared by sequential application of the *Stork-Danheiser* alkylation

Scheme 5



16 X = H, Br **5** **15** Trisyl = 2,4,6-triisopropyl-benzenesulfonyl

Table 2. *Divinyl Ketones* **1i–l** *from Trisylhydrazones* **15**[a])



[a]) Yields after chromatography; Trisyl = 2,4,6-triisopropylbenzenesulfonyl. [b]) *s*-BuLi. [c]) **6b**. [d]) NiO_2. [e]) **6c**. [f]) **6a**. [g]) $BaMnO_4$.

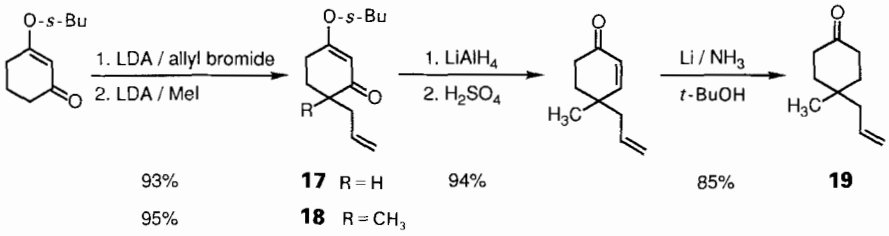
[10] (→**17**→**18**) as shown in *Scheme 6*[3]). Li in NH_3 selectively reduced the conjugated double bond. The alcohols **7i–l** were oxidized with either NiO_2 or $BaMnO_4$ as indicated in *Table 2*. The divinyl alcohol **7l** served as starting material also for the protected divinyl ketone **1m** *(Scheme 7)*: selective hydroboration of **7l** afforded the diol **20** which could be selectively oxidized to **21** with $BaMnO_4$ which was protected as the trichloroacetate **1m**.

The results of the direct formation of vinyllithium reagents **5** from **16** with metallating agents, of the subsequent reactions of **5** with **6a** to form **7n–q**, and of the oxidation to **1n–q** are collected in *Table 3*. $BaMnO_4$ proved to be the oxidant of choice. The bromo-olefins **22**, **24** (*via* **23**), and **26** (*via* **25**) were readily prepared as outlined in *Scheme 8* (see *Exper. Part*).

3. *Acyl Chloride and (β-Silylvinyl)cuprate.* A direct one-pot construction of divinyl ketones was briefly investigated using *Fleming*'s silylcupration method [12] (see *Scheme*

[3]) The *sec*-butyl ether was found to be superior to the ethyl or isobutyl ether in the *Stork-Danheiser* sequence.

Scheme 6



Scheme 7

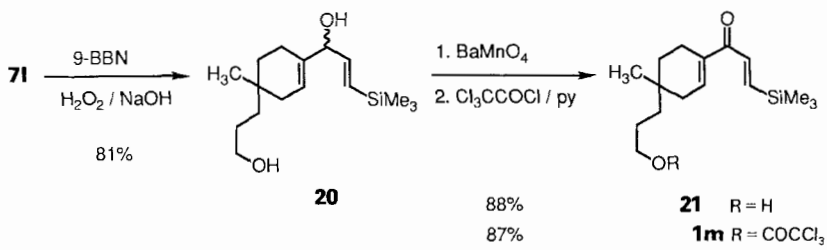
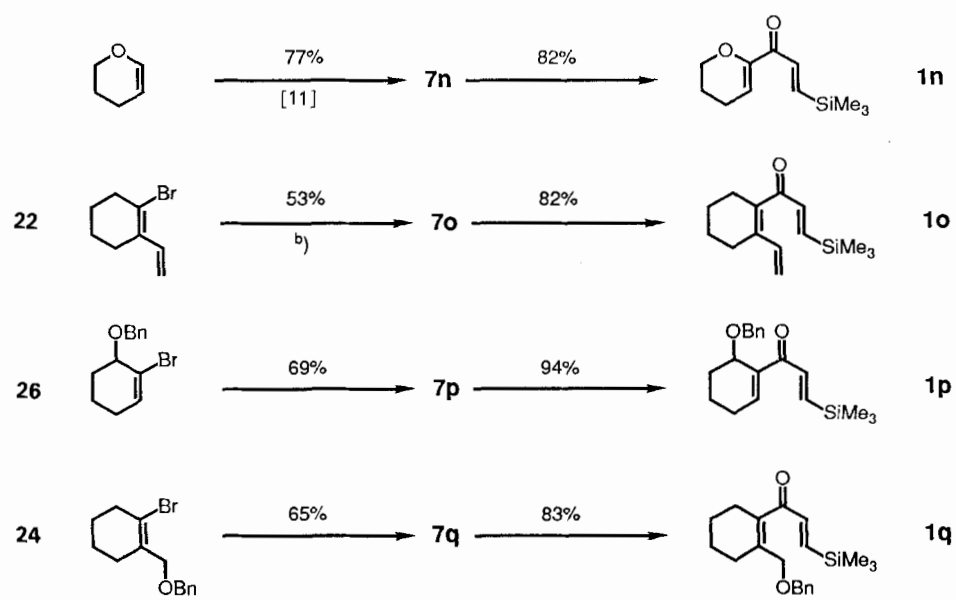


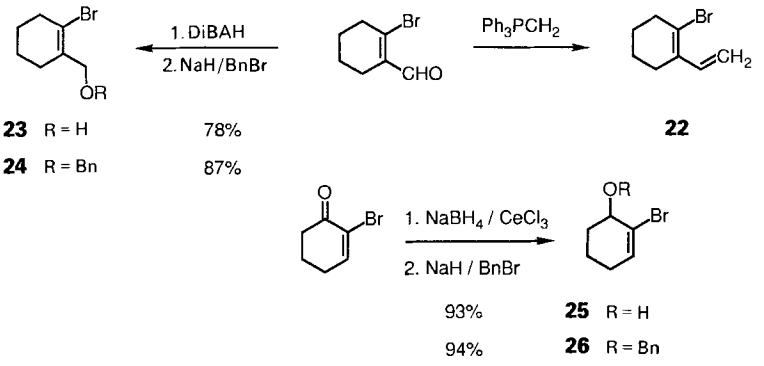
Table 3. *Divinyl Ketones* **1n–q** *from Vinyllithium Reagents* **5** *Generated by Deprotonation or Li/Br Exchange of* **16**



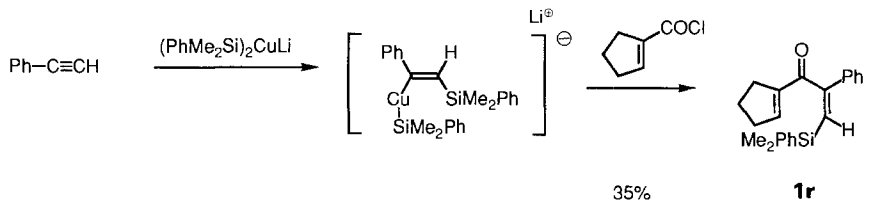
a) Yield after chromatography. In all cases, *t*-BuLi was used as base or metallating agent, **6a** as the electrophile, and $BaMnO_4$ as the oxidant.

b) BuLi was used.

Scheme 8



Scheme 9



9). The homocuprate prepared from (dimethylphenylsilyl)lithium added to phenylacetylene to generate an intermediate (β-silylvinyl)cuprate which coupled with cyclopentenecarbonyl chloride to provide divinyl ketone **1r** in 35% overall yield. The reaction was not further optimized.

Cyclization of Divinyl Ketones 1. – The eighteen divinyl ketones **1** employed in this study were selected to test various substituent effects on rate and compatibility of their cyclization (see *Scheme 1*). For clarity of discussion, they are separated into two classes: divinyl ketones 1) with C-substituents and 2) with heteroatom-containing substituents. In nearly every case, the use of anhydrous $FeCl_3$ in CH_2Cl_2 was found to be optimal. To aid the discussion of the configurational aspects, the pertinent ^{1}H-NMR data of the cyclization products **2** are given in *Table 4*.

1. *Divinyl Ketones with C-Substituents.* 1.1. *Saturated Substituents of the Vinyl Moieties.* The cyclization results are collected in *Table 5*. Ketone **1k** addresses no new questions and in its role as a control substrate, it cyclized to a single product with similar rate and yield as the parent compound [1b]. The ring-fusion configuration was established to be *cis* by hydrogenation of **2k** to a saturated ketone which produced a minor isomer upon base-catalyzed equilibration (ratio 86:14)[4]. In addition, the small value of $^2J(2,3a)$ (1.1 Hz) disqualifies the *trans*-fused isomer ($J(2,3a) = 2.5$–3.0 Hz) and indicates that the C=O group is axially disposed at C(7a) of the indanone [1c].

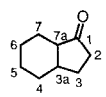
The ketone **1b** was investigated in the context of a total synthesis of punctatin [14] as well as in a study of its potential for cyclobutylmethyl-cation rearrangements [15].

[4]) The ratio for 1-indanone is *cis*/*trans* 75:15 [13].

Table 4. *Selected ^{1}H-NMR Data for Cyclization Products* **2**[a])

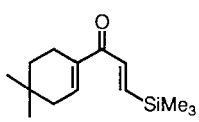
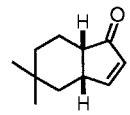
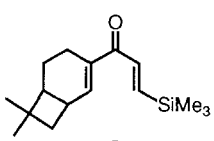
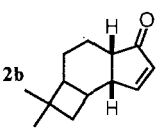
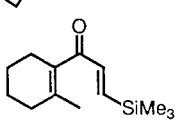
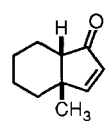
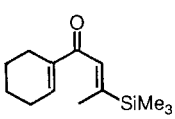
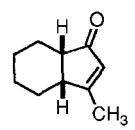
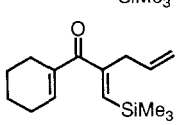
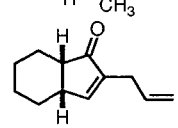
Compound	Chemical shifts δ [ppm]				Coupling constants J [Hz]			
	H–C(2)	H–C(3)	H–C(3a)	H–C(7a)	J(2,3a)	J(3,3a)	J(4,3a)	J(7a,3a)
2a	6.06	7.46	–	2.02	–	–	–	–
2b (*c,t*)	6.15	7.60	2.90	2.53	2.3	2.6	2.7	–
2b (*c,c*)	6.22	7.43	3.07	–	1.9	2.8	–	–
2c	6.11	7.72	3.25	2.88	1.5	2.8	5.8	6.8
2d	6.11	7.46	3.42	2.70	2.5	2.4	3.2	6.4
2e	6.34	7.59	4.75	2.37	1.1	2.6	–	(5.7)
2h	6.30	7.55	5.33	2.68	1.9	–	–	–
2i	5.79	–	2.69	2.37	0	–	–	–
2g	–	7.26	2.87	2.46	–	2.9	–	–
2k	6.11	7.69	3.02	2.38	1.1	3.0	–	–
2s	6.12	7.69	3.00	2.39	1.0	3.0	–	6.6
2s'	6.12	7.68	3.00	2.38	0	2.9	–	6.6

[a]) Arbitrary numbering for all cyclization products as given in the parent **A**:



A

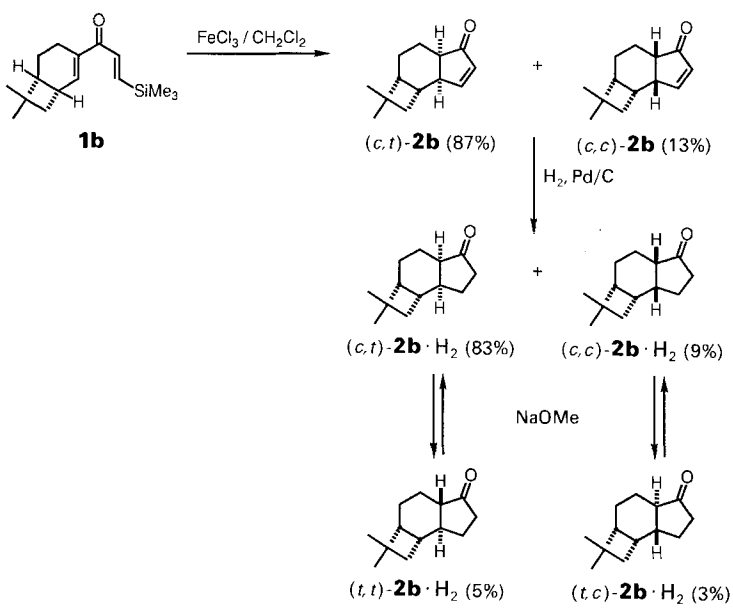
Table 5. *Cyclization of Divinyl Ketones with Saturated C-Substituents*[a])

Substrate	Time [h]	Temp. [°]	Product	*cis/trans*	Yield [%][b])
1k 	4	0	**2k** 	100:0	78
1b 	2	0	**2b** 	100:0[c])	40
	144	–25		100:0[c])	69
1a 	13	20	**2a** 	100:0	70
1i 	12	20	**2i** 	100:0	70
1j 	1	–25	**2j** 	100:0	76

[a]) All reactions were run at 0.08M in CH_2Cl_2 with 1.05 equiv. of $FeCl_3$.
[b]) Yield after chromatography.
[c]) See text and *Scheme 10* for discussion of configurations.

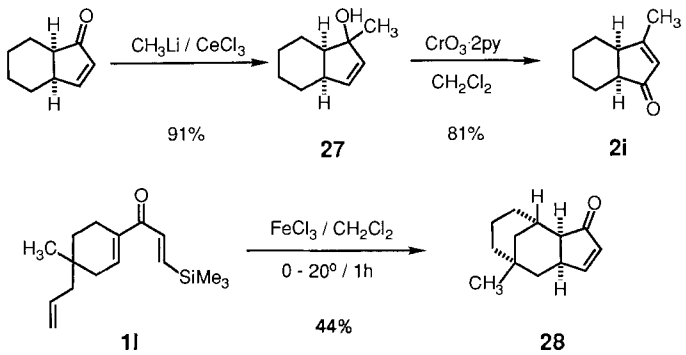
Reaction of **1b** with $FeCl_3$ at 0° was complete within 2 h and provided a modest yield of **2b** as a 5:1 mixture of isomers. Lowering the temperature to −25° improved both the yield (69%) and stereoselectivity (8:1). While we anticipated that the (*c*,*t*) isomer should predominate by previous analogy[5]), the perturbation induced by the fused cyclobutane ring weakened our confidence in the predictive model [1c] [1d]. Unambiguous assignment of the products could not be made by spectroscopic methods despite extensive one- and two-dimensional decoupling experiments. Ultimately, we resorted to conformational analysis, supported by MM2 calculations, as outlined in *Scheme 10*. The initial 87:13 mixture **2b** was hydrogenated to a 1:87:12 (elution order) mixture of ketones **2b**·H_2. Base-catalyzed equilibration produced a 5:83:3:9 mixture of isomers indicating that the first two isomers were interconverting as were the latter pair. The ability to interconvert implies the same relative configuration at C(3a) and C(4). MM2 calculations were performed to determine the relative energies of all possible conformations of each ketone isomer (**2b** and **2b**·H_2). It was found that at equilibrium, (*c*,*t*)-**2b**·H_2 is by 1.23 kcal/mol more stable than (*t*,*t*)-**2b**·H_2 corresponding to an 89:11 ratio (calc.) at 25°. Furthermore (*c*,*c*)-**2b**·H_2 is favored over (*t*,*c*)-**2b**·H_2 by only 0.59 kcal/mol (calc. ratio 73:27). Thus, the predicted equilibrium ratio for the *trans* family ((*c*,*t*)-**2b**·H_2 and (*t*,*t*)-**2b**·H_2) represents that observed (94:6) for the *major isomer*, while the ratio expected for the *cis* family ((*c*,*c*)-**2b**·H_2 and (*t*,*c*)-**2b**·H_2) is closer to that observed (75:25) with the minor isomer. Consequently, we assign (*c*,*t*)-**2b** and (*c*,*c*)-**2b** to the major and minor products of cyclization, respectively.

Scheme 10



[5]) The symbols *c* (*cis*) and *t* (*trans*) are used as stereochemical symbols. The 1st descriptor in a stereochemical symbol refers to the ring fusion, the 2nd to the relationship of H–C(3a) and the H at the remote chiral center (see [1c]: *c*/*t* corresponds to *C*/*T*).

Scheme 11



Substrates **1a** and **1i** bearing Me groups at C(β) both cyclized very sluggishly compared to the parent compound. It is notable that the yields remained high despite the decreased rate of reaction, and that no olefin isomers, ring fusion isomers, or other side products could be isolated. The *cis* configuration in **2a** was established by the hydrogenation/epimerization protocol which produced no new isomers. This is consistent with MM2 calculations which predict a 2.76 kcal/mol preference for *cis*-**2a** over *trans*-**2a** (*ca.* 99:1 at 25°)[6]). These calculations also show a clear preference for the conformation of the cyclohexane moiety with equatorial CH_3 and carbonyl groups. The structure of **2i** was confirmed by an independent synthesis as shown in *Scheme 11:* oxidative transposition [17] of the tertiary alcohol **27** (prepared by the selective 1,2-addition of $CH_3Li/CeCl_3$ [18]) proceeded poorly with the recommended chromium reagents (pyridinium chlorochromate, pyridinium dichromate, H_2CrO_4). Surprisingly, we found that freshly prepared *Collins* reagent [19] accomplished the desired reaction in excellent yield[7]).

The α-alkylated substrate **1j** underwent cyclization in less than 1 h at $-25°$ – a dramatic acceleration. Note that the allyl unit did not isomerize into conjugation suggesting that the double bond is not playing a role in the acceleration. The *cis* ring fusion is assumed by analogy. Finally, in view of the successful cyclizations of **1k** and **1j**, we anticipated nothing unusual from substrate **1l**. Reaction with $FeCl_3$ in CH_2Cl_2 occurred rapidly to give several products. The major component, isolated in 44% yield, was not the expected hydroindenone, but proved to be, after extensive spectroscopic analysis, the unusual bicyclo[3.3.1]nonane **28** *(Scheme 11)*. The details of the structural elucidation will be published elsewhere[8]).

1.2. *Unsaturated Substituents at the Vinyl Moieties.* The effects of conjugation at C(α) or C(β) of the divinyl ketone is nicely illustrated by comparison of the rates of cyclization of **1c** and **1d** (see *Table 6*) with the saturated system **1k**. Clearly, the redistribution of cationic character during the cyclization is manifested in these substrates[9]). The *cis* ring

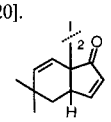
---

[6]) This conclusion has been corroborated recently [16].

[7]) This reagent is reported to give epoxyaldehydes with tertiary vinylic alcohols [20].

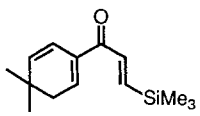
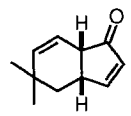
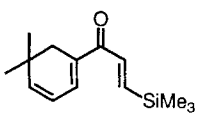
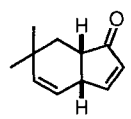
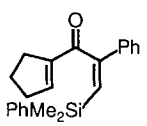
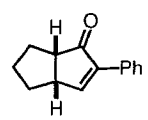
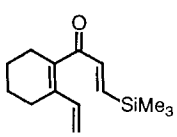
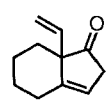
[8]) We have found this to be a general reaction and will describe studies on its mechanism as well as scope and limitations in a forthcoming paper.

[9]) A C(7a)-coupled dimer **29** of **2d** was isolated in 7% yield.



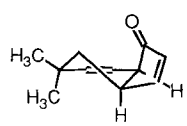
29

Table 6. *Cyclization of Divinyl Ketones with Unsaturated C-Substituents*[a])

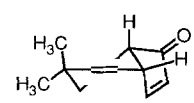
Substrate	Time [h]	Temp. [°]	Product	*cis*/*trans*	Yield [%][b])
1c 	1	–15	 **2c**	100:0	70[c])
1d 	2	20	 **2d**	100:0	69
1r 	3	–25	 **2r**	100:0	86
1o 	2	20	 **30**	–	44

[a]) All reactions were run at 0.08M in CH_2Cl_2.
[b]) Yield after chromatography.
[c]) 7% of a C(7a)-coupled dimer, **29**, was isolated.

fusions in **2c** and **2d** are assured by a ^2J(3a,7a) of 6.4–6.8 Hz. The allylic coupling constant ^3J(2,3a) of 1.5 Hz in **2c** indicates that the carbonyl group is in a pseudoaxial position in the cyclohexene half-chair. Interestingly, the ^3J(2,3a) of 2.5 Hz in **2d** suggests an equatorial position for the carbonyl moiety, thus avoiding an 1,3-diaxial interaction with a



2c

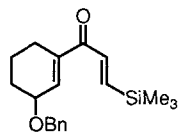
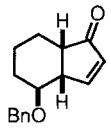
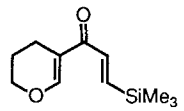
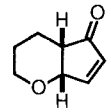
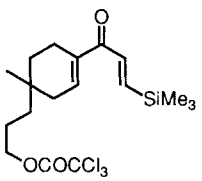
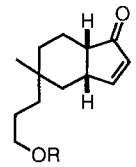
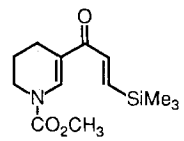
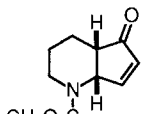


2d

pseudoaxial Me group. A more striking demonstration of the effects of α-conjugation is seen in the extremely facile cyclization of **1r**. By comparison, the unsubstituted substrate required 3 h at 25° and proceeded in only moderate (*ca.* 50%) yield [1b] [1d].

In an attempt to extrapolate our experience with substrates **1a** and **1d**, we anticipated a slow but successful cyclization of **1o**. However, we found that, while a hydroindenone was indeed produced, albeit in moderate yield, a skeletal rearrangement also took place affording the α-vinyl ketone **30**. We have investigated the mechanism of this anomalous

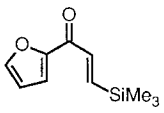
Table 7. *Cyclization of Divinyl Ketones with Heteroatom-Containing Substituents*[a])

Substrate	Time [h]	Temp. [°]	Product	*cis*/*trans*	Yield [%][b])
	2	0		100:0	76[c])
1e 	8	20	 **2e**	100:0	60
1m 	4	0[d])	 **2m** R = $COCCl_3$ **2s** R = H[f])	100:0[e])	78
1h 	36	60[g])	 **2h**	100:0[h])	76

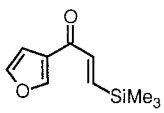
[a]) All reactions were run at 0.08M in CH_2Cl_2 with 1.05 equiv. of $FeCl_3$.
[b]) Yield after chromatography.
[c]) [1d].
[d]) 2.0 equiv. of $FeCl_3$ were used.
[e]) **2m** was formed as a 1:1 mixture of diastereoisomers.
[f]) **2s** was obtained by saponification of **2m**.
[g]) $ZnCl_4$ in 1,2-dichloroethane was used.
[h]) Configuration assigned by analogy.

cyclization by ^{13}C-labeling experiments. The reaction has a limited but interesting scope which is described in the accompanying paper.

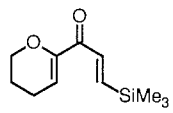
2. *Divinyl Ketones with Heteroatom-Containing Substituents.* We have examined a number of substrates containing ether, ester, and carbamate functions in various positions to evaluate their general compatibility with the cyclization conditions (see *Table 7*). The substrates **1f**, **1g**, **1n**, **1p**, and **1q** failed to cyclize *(vide infra)*. In a previous publication, we reported the successful cyclization of a divinyl ketone bearing a benzyl ether at C(3′) (first entry *Table 7*); no side-products were isolated and the reaction proceeded in high yield and with excellent stereoselectivity [1d]. However, substrate **1p** *with a benzyl*



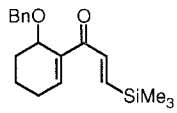
1f[a])



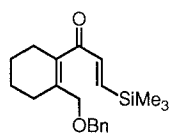
1g[a])



1n[a])



1p[a])



1q[a])

[a]) Not suitable for cyclization.

ether in the complementary 6′-position decomposed with $FeCl_3$, and only a 30% yield of the deprotected alcohol could be obtained. Replacement of the benzyl ether with a methyl ether, activation of the divinyl ketone by incorporation of an allyl group at C(2), and alternate *Lewis* acids were all explored without success. Equally surprising was the failure of substrate **1q** to cyclize. Treatment with a variety of *Lewis* acids led to deep-blue reaction mixtures and rapid decomposition suggesting aromatization of **1q**.

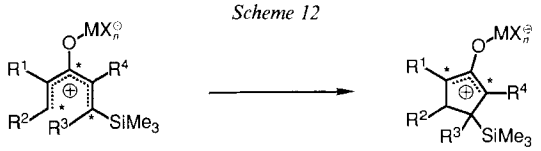
The regioisomeric dihydropyran substrates **1e** and **1n** behaved very differently. As we expected, **1e** reacted more slowly than its hydrocarbon parent (8 h at 20°), but the product could be obtained in 60% yield. The ^{1}H-NMR data support the assignment of a *cis* ring fusion with an axially disposed carbonyl group. Also according to expectation, **1n** reacted with many *Lewis* acids at $< -20°$, but under no circumstances could we identify a trace of the desired product. Neither of the furyl vinyl ketones **1f** and **1g** showed reactivity under the usual reaction conditions and only decomposed at elevated temperatures.

The compatibility of other O-functions was explored in protected forms of keto alcohol **21** *(Scheme 7)*. After establishing that neither the free alcohol nor its (*t*-Bu)Me_2Si ether withstood $FeCl_3$, we examined esters as protecting groups. The acetate, trifluoroacetate, and trichloroacetate of **21** could easily be prepared, and all cyclized cleanly with 2 equiv. of $FeCl_3$ (4 h, 0°). Each derivative survived the cyclization conditions, but the trichloroacetate **1m** was deemed superior, since it could be removed ($NaHCO_3$/EtOH) to form alcohol **2s** without effecting the cyclopentenone.

The ability to incorporate a protected N-function into the *Nazarov* cyclization was examined using the carbamate **1h**. We anticipated a profound retardation of the reaction due to the location of the donor atom and indeed found no reaction with $FeCl_3$ at ambient temperatures. Heating to 50° with $FeCl_3$ led only to decomposition. Through an extensive survey of reagents and conditions, we found that $ZrCl_4$ in CH_2Cl_2 (60°/36 h) efficiently promoted the reaction in good yield. Spectroscopic analysis of the product **2h** was complicated by the slow rotation of the carbamate function which broadened many of the resonances. Higher-temperature measurements achieved only partial coalescence.

Discussion. – Substituent influences on the rate of the SDNC were explored earlier using alkyl-substituted acyclic divinyl ketones [1b]. We observed that α- and α,β-substituted systems reacted much more rapidly than those with only β-substitution. Those results were interpreted to indicate that the rate-determining step of the reaction is the electrocyclization *(Scheme 12)*. Thus, when R^2 or R^3 are cation-stabilizing substituents, the reactant cation **iv** is selectively stabilized raising the activation energy for cyclization. Conversely, when R^1 or R^4 are cation-stabilizing substituents, the product cation **v** is selectively stabilized, thereby lowering the activation energy for the cyclization. Further, the accelerating effect of α-substitution was more pronounced than the decelerating influence of β-substitution. Since positive charge is more localized in the product cation **v**

Scheme 12



iv **v**

than in the starting cation **iv**, the effects of α-substitution are expected to be more profound. Although we discuss these effects in terms of the ground-state cation structures, their influence on the transition-state energy is also significant. An extensive discussion of the reactant-like or product-like nature of the transition state is not necessary because of the complementarity of charge distribution in the limiting cations. Thus, while reactant-stabilizing effects will also be present in the transition state, the effects *must be less significant* resulting in a net increase in ΔG (slower rate). This is necessarily true, because those effects are absent in the product cation. A similar argument can be made for product-cation stabilizing effects (faster rate).

The results of the present study are in complete accord with this picture. Alkyl substituents at either of the β-vinyl positions (**1a**, **1i**) markedly slowed the reaction. The interpretation here is, unfortunately, ambiguous, since both steric and electronic factors will act in the same sense. In the cases of α-vinyl substitution where the groups are remote from the bond-forming centers (**1j** and **1r**), striking rate enhancements were observed as these substrates cyclized at temperatures 25–50° lower than those required for the unsubstituted systems.

The substrates **1d** and **1c** provided a direct comparison of the α- and β-cation stabilizing effects of extended conjugation. The effects are substantial and in the expected directions. Overall, the SDNC is compatible with additional unsaturation in the substrate. Allyl and aryl groups at C(2) as well as vinyl and aryl groups at C(3') have been incorporated with no significant side reactions emerging. It is notable that in none of these cases did the ancillary double bond migrate into conjugation with the enone system. Clearly, the juxtaposition of unsaturated groups is not uniformly tolerated as **1l** and **1o** underwent alternative but interesting reactions.

The incorporation of heteroatoms in SDNC substrates offers an exacting test of the procedure's robustness by expanding the range of potential cationic side reactions. In addition, more extreme electronic effects are achievable, and new areas of synthetic utility are made available by employing heterocycles and heteroatomic appendages which embody synthetic potential. There seem to be no problems with the use of ethers, when they are removed from the site of action. Similarly, esters appear quite stable to the reaction conditions. The failure of cyclization of substrates with O-functions at C(α) may derive from debenzylation or β-elimination from the Fe(III) enolate **iii** for **1p** and chloride-induced opening of the oxonium ion **v** for **1n**[10]). The SDNC performs adequately with heteroatoms incorporated at the β-vinyl C-atom. With an O-atom in this position, the reaction is slow but otherwise unremarkable. In contrast, the carbamate function in **1h** exerts such a pronounced retarding effect that elevated temperatures are required for reaction. Under these circumstances, we recommend $ZrCl_4$ to avoid the oxidizing properties of Fe(III).

---

[10]) *Tius et al.* have recently made good use of a related oxonium-ion cleavage [21].

In summary, we have demonstrated the functional compatibility profile for the SDNC which simultaneously provides a basis for predicting the influence of other groups on the success *and* rate of the reaction. Further studies will define the utility of the SDNC in seven- and eight-membered ring systems as well as in the synthesis of linear tricyclic compounds.

We gratefully acknowledge the financial support for this project by a grant from the *National Science Foundation (Presidential Young Investigator Award)* and the *Alfred P. Sloan Foundation*. Matching funds for this project were provided by *The Upjohn Company*. This work was supported in part by the University of Illinois Mass Spectrometry Laboratory (PHS HHS GM 27029).

Experimental Part

1. General. – Melting points (m.p.): *Thomas-Hoover* capillary melting-point apparatus; corrected. Bulb-to-bulb distillations: *Büchi-GKR-50* Kugelrohr; boiling points (b.p.) refer to air-bath temp. and are uncorrected. Anal. TLC: *Merck* silica-gel plates with *QF-254* indicator; visualization with UV light, phosphomolybdic acid, I_2, vanillin and/or 2,4-dinitrophenylhydrazine soln.; R_f data for the following systems: hexane/AcOEt or pentane/Et_2O. Column chromatography: method of *Still* [2] (33–63 μm silica gel, *Woelm*). Anal. GC: *Varian-3700* chromatograph fitted with a flame-ionization detector (N_2 carrier gas for packed columns, 30 ml/min; H_2 for capillary columns, 1 ml/min); column *A:* 50 m *OV-17 WCOT*, split ratio 30:1; column *B:* 50 m *OV-1 WCOT*, split ratio 50:1; retention times (t_R) and integrals from a *Hewlett Packard 3390* recorder. BuLi, *s*-BuLi, and *t*-BuLi were titrated according to the method of *Gilman*. Brine refers to a sat. aq. NaCl soln. All reactions were performed in oven (140°) or flame-dried glassware under dry N_2. IR spectra: *Perkin-Elmer 1320, Nicolet 7199C* FT-IR, or *IBM IR/32* FT-IR spectrometer as thin films between NaCl plates, unless otherwise stated; in cm^{-1}. ^{1}H-NMR spectra: *Varian EM-390* (90 MHz), *XL-200* (200 MHz), *General Electric QE-300* (300 MHz), or *Nicolet NTC-360* (360 MHz) spectrometers in $CDCl_3$ with either tetramethylsilane (TMS, 0.00 ppm), CH_2Cl_2 (5.33 ppm), or $CHCl_3$ (7.26 ppm) as internal standard; chemical shifts (δ) in ppm, coupling constants J in Hz. ^{13}C-NMR spectra: *General Electric QE-300* (75.5 MHz) using $CDCl_3$ (δ77.05) as internal reference. MS: *Finnigan-MAT-CH-5* spectrometer with an ionization voltage of 70 eV; in m/z (intensity relative to base = 100). HR-MS: *Finnigan-MAT-731* spectrometer. Capillary GC-MS spectra: *Finnigan-VG-7070E* spectrometer. Elemental analyses: University of Illinois Microanalytical Service Laboratory.

2. Starting Materials. – (*E*)-2-(Bromoethenyl)trimethylsilane [3], 3-(trimethylsilyl)-2-propenal and 3-(trimethylsilyl)-2-propyn-1-ol [2], 2-methylcyclohexenecarboxaldehyde (**3a**) [23a], 4,4-dimethyl-1,5-cyclohexadienecarboxaldehyde (**3c**) [2b], 3,4-dihydro-2*H*-pyran-5-carboxaldehyde (**3e**) [23b], methyl 5-formyl-1,2,3,4-tetrahydropyridine-1-carboxylate (**3h**) [23c], 4,4-dimethyl-2-cyclohexenone [23d], 1-bromo-2-ethenyl-1-cyclohexene (**22**) [23c], *cis*-7,7-dimethylbicyclo[4.2.0]octan-2-one [23f], 2-bromo-2-cyclohexenone [23g], 2-bromo-1-cyclohexenecarboxaldehyde [23h], and 6-(methoxymethylidene)-4,4-dimethyl-2-cyclohexenone (**9**) [23i], and 3-[(2-methylpropyl)oxy]-2-cyclohexenone [23j] were all prepared by literature methods.

3. Synthesis of Precurors. – 3.1. *Preparation of Enals. 7,7-Dimethyl-*cis*-bicyclo[4.2.0]oct-2-ene-3-carboxaldehyde* (**3b**). NaH (1.85 g of 55% dispersion, 42.0 mmol) under N_2 was covered with Et_2O (70 ml), and EtOH (0.175 ml) was added. The mixture was cooled in an ice bath and 7,7-dimethyl-*cis*-bicyclo[4.2.0]octan-2-one (5.33 g, 35 mmol) and ethyl formate (4.3 ml, 52.5 mmol) were added together in 15 ml of anh. Et_2O dropwise within 45 min under stirring. The resulting slurry was warmed to r.t., stirred for 12 h, cooled in an ice bath, and quenched with 5 ml of EtOH and 50 ml of H_2O. The org. layer was washed with 30 ml of H_2O, and the aq. layers were washed with 30 ml of Et_2O. The combined aq. layers were acidified with 6M HCl and then extracted with Et_2O (3 × 150 ml). The org. layers were washed with brine (50 ml), dried ($MgSO_4$), evaporated, and distilled to yield 5.95 g (94%) of *3-(hydroxymethylidene)-7,7-dimethyl-*cis*-bicyclo[4.2.0]octan-2-one*. B.p. 100°/2 Torr. IR (neat): 2950*s*, 2863*m*, 1640*s*, 1586*s*, 1455*m*, 1370*m*, 1310*m*, 1269*m*, 1221*m*, 1184*m*, 1152*m*, 895*m*. ^{1}H-NMR (200 MHz): 14.33 (br., OH), 8.33 (br. *d*, J = 2.0, H–C(9)); 3.06 (*q*, J = 8.9, H–C(1)); 2.39 (*ddd*, J = 14.5, 5.5, 4.0, H–C(6)); 2.15 (*m*, H–C(8), 2 H–C(4)); 1.94 (*m*, H–C(8)); 1.86–1.66 (*m*, 2 H–C(5)); 1.22 (*s*, CH_3); 0.98 (*s*, CH_3).

The hydroxymethylidene ketone (5.87 g, 32.6 mmol) in benzene (65 ml), i-BuOH (3.3 ml, 35.8 mmol), and TsOH (6 mg, 0.032 mmol) were refluxed for 14 h using a *Dean-Stark* apparatus to separate H_2O. The mixture was

cooled and washed with 1M NaOH (30 ml), H_2O (50 ml), and brine (50 ml). The org. phase was dried ($MgSO_4$), filtered, concentrated, and distilled to afford 6.49 g (84%) of *3-(isobutoxymethylidene)-7,7-dimethyl-*cis*-bicyclo-[4.2.0]octan-2-one* (**8**). B.p. 125°/0.05 Torr. R_f 0.37 (hexane/AcOEt 3:1). IR (neat): 2957*s*, 2867*s*, 1715*m*, 1676*s*, 1595*s*, 1470*m*, 1397*w*, 1383*w*, 1368*w*, 1293*m*, 1202*s*, 1144*s*, 1098*s*, 1065*m*, 1001*m*, 909*w*, 797*w*, 662*w*. ^{1}H-NMR (300 MHz): 7.32 (*m*, H–C(9)); 3.76 (*d*, *J* = 6.7, 2 H–C(10)); 2.94 (*q*, *J* = 9.0, H–C(1)); 2.70 (*dt*, *J* = 15.6, 4.3, H–C(6)); 2.28–2.16 (*m*, 2 H–C(4)); 2.13–2.04 (*m*, H–C(8)); 1.95 (*m*, 2 H–C(11)); 1.80–1.70 (*m*, H–C(5)); 1.65–1.58 (*m*, H–C(5)); 1.18 (*s*, CH_3); 0.95 (*s*, CH_3); 0.93 (*d*, *J* = 6.7, 2 CH_3). ^{13}C-NMR (75.5 MHz): 204.0 (C(2)); 155.7 (C(9)); 115.6 (C(3)); 81.0 (C(1)); 44.2 (C(6)); 38.0 (C(1), C(8)); 35.0 (C(7)); 29.7 (CH_3–C(7)); 28.9 (C(11)); 23.8 (CH_3–C(7)); 22.4 (C(5)); 21.9 (C(4)); 18.7 (2 CH_3). MS: 236 (26, M^+), 181 (10), 180 (37), 168 (16), 137 (23), 125 (43), 124 (70), 123 (21), 112 (35), 111 (21), 109 (25), 107 (13), 106 (73), 105 (81), 96 (11), 95 (37), 83 (17), 79 (15), 78 (13), 77 (13), 69 (15), 67 (19), 57 (100), 56 (16), 55 (27), 53 (120), 43 (16), 41 (99), 39 (23), 31 (11), 30 (16), 28 (70). Anal. calc. for $C_{15}H_{24}O_2$: C 76.23, H 10.24; found: C 76.09, H 10.34.

To a mixture of **8** (6.50 g, 27.5 mmol) and $CeCl_3 \cdot 7\ H_2O$ (10.24 g, 27.5 mmol) in MeOH (140 ml) at −40°, $NaBH_4$ (1.04 g, 27.5 mmol) was added cautiously (foaming) in portions over 15 min, keeping the temp. below −30°. The mixture was stirred for 2 h at −40° and then quenched with 75 ml of 1M HCl. After the mixture had warmed up, it was diluted with brine (200 ml) and extracted with Et_2O (3 × 200 ml). The org. layers were washed with brine (2 × 100 ml), combined, dried ($MgSO_4$), filtered, evaporated, and chromatographed to afford 2.19 g (48%) of **3b**. B.p. 65°/0.1 Torr. R_f 0.33 (hexane/AcOEt 8:1). IR (neat): 2932*s*, 2863*s*, 2807*m*, 2712*w*, 1686*s*, 1632*s*, 1455*m*, 1368*m*, 1291*w*, 1271*w*, 1236*w*, 1184*m*, 1159*w*, 1140*m*, 1111*w*, 999*w*, 955*m*, 847*w*, 758*w*, 710*w*. ^{1}H-NMR (300 MHz): 9.38 (*s*, CHO); 6.76 (*dd*, *J* = 4.0, 1.8, H–C(2)); 3.06 (*ddt*, *J* = 18.7, 9.5, 2.9, H–C(1)); 2.49 (*dt*, *J* = 16.3, 3.9, H–C(4)); 2.11–2.04 (*m*, H–C(4)); 1.99 (*ddd*, *J* = 10.7, 9.1, 2.9, H–C(6)); 1.84–1.72 (*m*, H–C(8), H–C(5)); 1.72 (*q*, *J* = 10.2, H–C(8)); 1.56–1.47 (*m*, H–C(5)); 1.22 (*s*, CH_3); 0.94 (*s*, CH_3). ^{13}C-NMR (75.5 MHz): 193.8 (C(9)); 154.6 (C(2)); 142.2 (C(3)); 43.0 (C(6)); 40.4 (C(8)); 34.5 (C(7)); 30.0 (C(1)); 29.5 (CH_3); 24.1 (CH_3); 22.0 (C(5)); 19.1 (C(4)). MS: 164 (0.6, M^+), 108 (77, $M^+ - (CH_3)_2C{=}CH_2$), 107 (58), 80 (14), 79 (100), 77 (23), 69 (25), 41 (38), 39 (18). Anal. calc. for $C_{11}H_{16}O$: C 80.44, H 9.82; found: C 80.52, H 9.87.

5,5-Dimethyl-1,3-cyclohexadienecarboxaldehyde (**3d**). To ketone **9** (0.834 g, 5.0 mmol) in MeOH (13 ml) at 0°, $CeCl_3 \cdot 7\ H_2O$ (1.87 g, 5.0 mmol) was added. $NaBH_4$ (0.209 g, 5.5 mmol) was then added in portions within 15 min, while keeping the temp. below 5°. After 5 min, the mixture was quenched with 1N HCl (3 ml), diluted with H_2O (50 ml), and extracted with Et_2O (3 × 100 ml). The org. extracts were washed with brine (2 × 50 ml), dried (K_2CO_3), filtered, and evaporated. Chromatography afforded **10** (0.277 g), **3d** (0.064 g), and **11** (0.150 g). Acetal **10** was converted to **3d** upon treatment with 0.1N HCl in THF (0°, 30 min). Alcohol **11** was oxidized to **3d** using $BaMnO_4$.

5,5-Dimethyl-1,3-cyclohexadienecarboxaldehyde Dimethyl Acetal (**10**): R_f 0.58 (hexane/AcOEt 5:1). ^{1}H-NMR (200 MHz) 5.97 (*m*, 1 H); 5.80 (*dd*, *J* = 8.8, 4.6, 1 H); 5.55 (*d*, *J* = 8.8, 1 H); 4.60 (*s*, 1 H); 3.30 (*s*, 6 H); 2.10 (*d*, *J* = 1, 2 H); 1.00 (*s*, 6 H).

5,5-Dimethyl-1,3-cyclohexadienemethanol (**11**): R_f 0.28 (hexane/AcOEt 3:1). IR (neat): 3305. ^{1}H-NMR (200 MHz): 5.80 (*m*, 2 H); 5.50 (*dd*, *J* = 8.4, 2.0, 1 H); 4.09 (*s*, 2 H); 2.06 (*d*, *J* = 1.3, 2 H); 1.58 (br., 1 H); 1.00 (*s*, 6 H).

3d: B.p. 95°/15 Torr. R_f 0.33 (hexane/AcOEt 8:1). IR (CCl_4): 2961*s*, 2928*m*, 2872*m*, 2818*w*, 2716*w*, 1688*s*, 1566*w*, 1468*m*, 1429*w*, 1390*w*, 1368*m*, 1293*w*, 1213*m*, 1143*m*, 1026*m*. ^{1}H-NMR (300 MHz): 9.53 (*s*, CHO); 6.76–6.72 (*m*, H–C(2)); 6.05 (*m*, H–C(3), H–C(4)); 2.33 (*s*, 2 H–C(6)); 1.02 (*s*, 2 CH_3). GC-MS: 136 (46, M^+), 121 (48), 107 (33), 93 (100), 91 (83), 79 (23), 77 (70), 65 (28), 51 (21), 41 (18), 39 (30). HR-MS: 136.0887 ($C_9H_{12}O$, calc. 136.0888).

3.2. *Preparation of β-Silylpropenals. 3-Iodo-3-(trimethylsilyl)-2-propen-1-ol* (**12**). To a 3.4M soln. of sodium bis(2-methoxyethoxy)aluminum hydride in toluene (0.16 mol) and Et_2O (60 ml) at 0°, a soln. of 3-(trimethylsilyl)-2-propyn-1-ol (12.83 g, 0.10 mol) in Et_2O (60 ml) was added dropwise within 20 min. After 10 min stirring, the soln. was permitted to warm to r.t. When GC analysis indicated the silyl propargylic alcohol had disappeared, the soln. was cooled to 0° and AcOEt (17.6 g, 0.20 mol) added to quench residual hydride. After 10 min at 0°, the soln. was cooled to −78° and I_2 (76.1 g, 0.30 mol) added in small portions. The mixture was allowed to warm to r.t. Sat. NH_4Cl soln. (400 ml) was added and the mixture extracted with Et_2O (3 × 1 l). The individual org. extracts were washed with 1M $Na_2S_2O_3$ (2 × 400 ml) and brine (1 × 400 ml), pooled and dried ($MgSO_4$), and evaporated. Chromatography and bulb-to-bulb distillation provided 17.09 g (67%) of **12** as a yellow-red liquid. GC (*pOV-101 12'*; 75° 5 min, 15°/min, 290°): 3-(trimethylsilyl)propyn-1-ol t_R 9.1 min, (*E*)-3-(trimethylsilyl)-2-propen-1-ol (quenched intermediate product of reduction) t_R 8.6 min, 3-iodo-3-(trimethylsilyl)-2-propen-1-ol t_R 15.0 min. IR (CCl_4): 3355*s*, 2959*s*, 2899*m*, 2363*w*, 1719*m*, 1653*m*, 1611*m*, 1559*m*, 1539*w*, 1447*m*, 1406*m*, 1375*m*, 1350*m*, 1248*s*, 1030*s*, 968*m*, 880*s*. ^{1}H-NMR (200 MHz): 6.48 (*t*, *J* = 4.8, H–C(2)); 4.25 (*d*, *J* = 4.8, 2 H–C(1)); 2.02–1.95 (br. *s*, OH); 0.18 (*s*, Me_3Si).

3-(Trimethylsilyl)-2-buten-1-ol (**13**). A 1.26M soln. of CH_3Li (95 ml, 0.12 mol) was added to dry CuCN (5.37, 0.06 mol) in Et_2O (60 ml) at 0°. After stirring for 10 min, a soln. of **12** (6.895 g, 0.0269 mol) in Et_2O (20 ml) was added. The mixture was stirred at 0° for 26 h (TLC monitoring). Sat. NH_4Cl soln. (130 ml) was carefully added and the mixture extracted with Et_2O (3 × 260 ml). The individual extracts were washed with H_2O (2 × 130 ml) and brine (1 × 130 ml), dried (K_2CO_3), and evaporated. Distillation secured 3.30 g (85%) of **13**. IR (CCl_4): 3854*w*, 3623*w*, 3343*w*, 2954*s*, 1937*w*, 1717*w*, 1653*w*, 1622*w*, 1559*w*, 1443*w*, 1404*w*, 1377*m*, 1304*w*, 1248*s*, 1121*w*, 1065*m*, 1009*m*. ^{1}H-NMR (200 MHz): 5.89–5.86 (*m*, H–C(2)); 4.25 (br. *s*, 2 H–C(1)); 1.70 (*t*, *J* = 0.95, CH_3); 0.06 (*s*, Me_3Si). MS: 144 (1.5, $M^{+\cdot}$), 129 (36, $M^{+\cdot}$ – Me), 75 (83), 73 (100, Me_3Si), 59 (11), 53 (34), 45 (19), 43 (18), 39 (11).

3-(Trimethylsilyl)-2-butenal (**6b**). To a soln. of pyridinium chlorochromate (3.88 g, 18 mmol) and anh. Na_2SO_4 (0.295 g, 3.6 mmol) in CH_2Cl_2 (15.5 ml), **13** (1.73 g, 12 mmol) was added in one portion and the resulting dark mixture stirred at r.t. After 15 min, *Celite* (5 g) was added and stirring was continued for 5 min. The mixture was diluted with Et_2O (150 ml) and filtered through a pad of *Celite*, and the pad was washed with 3 75-ml portions of Et_2O. The Et_2O soln. was concentrated and distilled (bulb-to-bulb) to provide 1.309 g (77%) of **6b**. A small-scale oxidation gave a greater than 83% yield. IR (neat): 2959*s*, 2853*m*, 2741*m*, 2361*w*, 1711*vs*, 1676*m*, 1611*m*, 1559*w*, 1539*w*, 1522*w*, 1507*m*, 1437*m*, 1408*m*, 1370*w*, 1250*vs*, 1167*m*, 1130*m*, 1069*s*, 992*m*, 947*s*. ^{1}H-NMR (200 MHz): 10.10 (*d*, *J* = 7.9, CHO); 6.19 (*dd*, *J* = 7.7, 1.0, H–C(2)); 2.23 (*d*, *J* = 1.6, CH_3); 0.13 (*s*, Me_3Si).

2-(Trimethylsilylmethylidene)-4-penten-1-ol (**14**). Prepared according to [8]. Yield 61%. B.p. 115°/25 Torr. IR (neat): 3333*s*, 3081*m*, 3006*m*, 2955*s*, 2897*s*, 1935*w*, 1833*w*, 1624*s*, 1435*s*, 1294*m*, 1248*vs*, 1140*m*, 1090*s*, 1040*s*, 994*s*, 914*s*. ^{1}H-NMR (200 MHz): 5.84–5.70 (*m*, H–C(4)); 5.61 (*d*, *J* = 1, H–C(1′)); 5.12–5.00 (*m*, 2 H–C(5)); 4.06 (*s*, 2 H–C(1)); 2.92 (*dd*, *J* = 6.5, 1.4, 2 H–C(3)); 1.61–1.51 (br. *s*, OH); 0.13 (*s*, Me_3Si). MS: 170 (0.4, $M^{+\cdot}$), 155 (14, $M^{+\cdot}$ – Me), 137 (10), 75 (100), 73 (56, Me_3Si), 61 (16), 59 (17), 45 (20), 43 (14). Anal. calc. for $C_9H_{18}OSi$: C 63.46, H 10.65, Si 16.49; found: C 63.38, H 10.44, Si 16.43.

2-(Trimethylsilylmethylidene)-4-pentenal (**6c**). To a mechanically stirred mixture of pyridinium chlorochromate (16.17 g, 0.075 mol) and NaOAc (1.23 g, 0.015 mol) in CH_2Cl_2 (60 ml) under N_2, **14** (0.05 mol) was added at r.t. TLC indicated the reaction was over within 10 min. The mixture was diluted with 590 ml Et_2O; the supernatant was decanted and the residue washed with Et_2O (3 × 160 ml). The soln. was passed through a plug of *Florisil*, the filtrate concentrated, and the crude product distilled to yield 68% of **6c** B.p. 113–115°/25 Torr. IR (neat): 3359*m*, 2997*m*, 2957*s*, 2902*m*, 2801*m*, 2365*w*, 1945*w*, 1690*vs*, 1640*s*, 1597*m*, 1559*w*, 1428*m*, 1343*m*, 1300*m*, 1250*s*, 1223*m*, 1146*w*, 1127*m*, 1096*m*, 995*s*, 912*s*. ^{1}H-NMR (200 MHz): 9.41 (*s*, CHO); 6.78 (*s*, H–C(1)); 5.82–5.73 (*m*, H–C(4)); 5.02 (*s*, H–C(5)); 4.98–4.92 (*m*, J_{trans} = 7.6, H–C(5)); 3.10 (*d*, *J* = 6.0, 2 H–C(3)); 0.06 (*s*, Me_3Si). MS: 168 (0.45, $M^{+\cdot}$), 153 (39, $M^{+\cdot}$ – CH_3), 125 (18), 75 (75), 73 (100, Me_3Si^+), 61 (19), 59 (26), 45 (24), 43 (24). Anal. calc. for $C_9H_{16}Si$: C 62.22, H 9.58, Si 16.69; found: C 63.97, H 9.36, Si 17.04.

3.3. *Preparation of Vinyl Bromides. 1-Benzyloxy-2-bromo-2-cyclohexene* (**26**). To 2-bromo-2-cyclohexenone (12.7 g, 72.6 mmol) in MeOH (180 ml) and $CeCl_3 \cdot 7\ H_2O$ (27.04 g, 72.6 mmol), $NaBH_4$ (2.75 g, 72.6 mmol) was added cautiously due to foaming. After 5 min, the mixture was neutralized with 1N HCl, diluted with H_2O (400 ml), and extracted with Et_2O (3 × 200 ml). The extracts were washed with H_2O (150 ml) and brine (150 ml). The org. layers were combined, dried (K_2CO_3), evaporated, and distilled to give 11.96 g (93%) of *2-bromo-2-cyclohexen-1-ol* (**25**) as a colorless solid. M.p. 37–39°.

NaH (0.31 g, 50% dispersion, 6.34 mmol) was washed with hexane (3 × 3 ml), covered with THF (5 ml), and cooled to 0°. A soln. of **22** (1.02 g, 5.76 mmol) in 5 ml of THF was added and the resulting yellow slurry warmed to r.t. and then cooled to 0°. Bu_4NI (0.21 g, 0.58 mmol) and benzyl bromide (0.69 ml, 5.76 mmol) were added, and the mixture was allowed to warm to r.t. After 30 min, the milky soln. was poured into H_2O (50 ml) and extracted with Et_2O (3 × 25 ml). The org. layers were washed with H_2O (2 × 25 ml) and brine (25 ml), dried (K_2CO_3), evaporated, and chromatographed to yield 1.44 g (94%) of **26**. B.p. 95°/0.05 Torr. R_f 0.34 (hexane/AcOEt 10:1). IR (neat): 3080*w*, 3060*m*, 3030*m*, 2930*s*, 2860*s*, 2830*s*, 1640*w*, 1495*m*, 1450*s*, 1435*m*, 1425 (sh), 1390*m*, 1350*s*, 1330*s*, 1305 (sh), 1250*m*, 1200*m*, 1175*m*, 1160*s*, 1080*s*, 1055*s*, 1025*s*, 980*s*, 965*s*, 930*s*, 870*w*, 845*w*, 805*m*, 750 (sh), 735*s*, 695*s*, 620*m*. ^{1}H-NMR (360 MHz): 7.43–7.26 (*m*, Ph); 6.25 (*t*, *J* = 4.0, H–C(3)); 4.68 (*d*, *J* = 1.6, 1 H, CH_2O); 4.63 (*d*, *J* = 1.6, 1 H, CH_2O); 3.97 (*d*, *J* = 2.8, H–C(1)); 2.13–1.57 (*m*, 2 H–C(4), 2 H–C(5), 2 H–C(6)). MS: 177 (12, $M^{+\cdot}$ – $PhCH_2$), 175 (12), 92 (47), 91 (100), 81 (16), 79 (32), 77 (15), 65 (13). Anal. calc. for $C_{13}H_{15}BrO$: C 58.45, H 5.65, Br 29.91; found: C 58.67, H 5.93, Br 29.94.

2-Bromo-1-cyclohexenemethanol (**23**). To a soln. of 2-bromo-1-cyclohexenecarboxaldehyde (2.16 g, 11.4 mmol) in THF (25 ml) at –78°, DIBAH (12.5 ml of 1.0M soln. in CH_2Cl_2) was added and the mixture stirred for 30 min. After addition of MeOH (3.5 ml), the mixture was warmed up and neutralized with 1N HCl and diluted with H_2O (50 ml). The mixture was extracted with Et_2O (3 × 100 ml). The org. phases were washed with brine (2 × 50 ml), combined, dried (K_2CO_3), filtered, evaporated, and chromatographed to yield 1.70 g (78%) of **23**. B.p. 85°/1

Torr. R_f 0.31 (hexane/AcOEt 3:1). IR (neat): 3308*s*, 2932*s*, 2861*s*, 2840*m*, 1657*w*, 1447*m*, 1435*m*, 1333*m*, 1267*w*, 1242*w*, 1175*w*, 1138*w*, 1105*m*, 1067*w*, 1013*s*, 970*m*, 797*m*, 667*m*. ^{1}H-NMR (300 MHz): 4.21 (*s*, 2 H–C(7)); 2.49 (*m*, 2 H–C(3)); 2.25 (*m*, 2 H–C(6)); 1.84 (br. *s*, OH); 1.68 (*m*, 2 H–C(4), 2 H–C(5)). ^{13}C-NMR (75.5 MHz): 135.3 (C(1)); 121.4 (C(2)); 66.3 (C(7)); 36.6 (C(3)); 29.1 (C(6)); 24.6 (C(4)); 22.3 (C(5)). MS: 192 (8), 190 (8, $M^{+\cdot}$), 111 (64), 93 (63), 91 (19), 81 (25), 79 (28), 77 (39), 67 (100), 65 (10), 57 (14), 55 (38), 53 (23), 52 (10), 51 (17), 43 (27), 41 (38), 39 (31), 31 (12). Anal. calc. for $C_7H_{11}BrO$: C 44.00, H 5.80, Br 41.82; found: C 43.90, H 5.81, Br 41.72.

1-(Benzyloxymethyl)-2-bromo-1-cyclohexene (**24**). Alcohol **23** was protected as the benzyl ether according to the aforementioned procedure. Yield 2.10 g (87%). B.p. 120°/0.05 Torr. R_f 0.35 (hexane/AcOEt 12:1). IR (neat): 3063*w*, 3032*w*, 2934*s*, 2860*s*, 1705*w*, 1680*w*, 1659*w*, 1497*w*, 1452*m*, 1435*w*, 1358*w*, 1333*w*, 1267*w*, 1203*w*, 1115*m*, 1072*s*, 1028*w*, 972*m*, 798*w*, 721*m*, 669*m*. ^{1}H-NMR (300 MHz): 7.38–7.27 (*m*, Ph); 4.49 (*s*, 2 H–C(8)); 4.19 (*s*, 2 H–C(7)); 2.52 (*m*, 2 H–C(3)); 2.25 (*m*, 2 H–C(6)); 1.68 (*m*, 2 H–C(4), 2 H–C(5)). ^{13}C-NMR (75.5 MHz): 138.4 (C(9)); 133.2 (C(1)); 128.3 (C(10)); 127.7 (C(11)); 127.5 (C(12)); 122.0 (C(2)); 73.2 (C(7)); 72.1 (C(8)); 36.8 (C(3)); 28.9 (C(6)); 24.7 (C(4)); 22.2 (C(5)). MS: 201 (5, $M^{+\cdot}$ – Br), 191 (4), 189 (4), 109 (5), 95 (13), 93 (10), 92 (45), 91 (100), 81 (39), 79 (17), 77 (15), 65 (12), 39 (10). Anal. calc. for $C_{14}H_{17}BrO$: C 59.80, H 6.09, Br 28.42; found: C 60.14, H 6.22, Br 28.64.

3.4. *Preparation of Trisylhydrazones. 4,4-Dimethylcyclohexanone (2,4,6-Triisopropylbenzenesulfonyl)hydrazone* (**15b**). Prepared by the method of *Bond* and coworkers [9]. Yield 77%. M.p. 115–117° (dec.). Anal. calc. for $C_{23}H_{38}N_2O_2S$: C 67.92, H 9.44, N 6.89, S 7.88; found: C 67.56, H 9.53, N 6.77, S 7.83.

4-Methyl-4-(2-propenyl)cyclohexanone (**19**) was prepared by the following sequence:

3-[(1-Methylpropyl)oxy]-6-(2-propenyl)-2-cyclohexen-1-one (**17**). To a soln. of (i-Pr)$_2$NH (68.6 g, 0.68 mol) in THF (400 ml) at –20° was added 2.5M BuLi (284 ml, 0.71 mol) in hexane. The mixture was stirred for 20 min at –20°, then cooled to –78°. 3-[(1-Methylpropyl)oxy]-2-cyclohexen-1-one (114 g, 0.68 mmol) was added in THF (170 ml) within 1.5 h and the resulting enolate stirred for 45 min at –78°. Allyl bromide (90.2 g, 0.74 mol) was added within 20 min in THF (140 ml). The mixture was permitted to warm to r.t. The soln. was cooled to 0° and the enolate quenched with 10 ml of H_2O. The soln. was concentrated and the residue extracted twice with Et_2O (670 ml) from brine (100 ml). The org. extracts were washed sequentially with H_2O (150 ml) and brine (150 ml), dried (K_2CO_3), and evaporated. Distillation afforded 131.5 g (93%) of **17**. B.p. 119–123°/1.3 Torr. IR (CCl_4): 3403*s*, 3080*m*, 2978*s*, 2938*m*, 2880*m*, 1656*s*, 1605*s*, 1454*m*, 1427*m*, 1384*s*, 1378*s*, 1335*m*, 1306*m*, 1264*s*, 1238*m*, 1214*s*, 1191*s*, 1171*s*, 1121*s*, 1095*m*. ^{1}H-NMR (300 MHz): 5.71–5.63 (*m*, C*H*=CH$_2$); 5.21 (*s*, H–C(2)); 4.98–4.90 (*m*, CH=C*H*$_2$); 4.08 (*m*, OC*H*); 2.56–2.51 (*m*, H–C(6)); 2.29 (*t*, J = 5.1, C*H*$_2$CH=CH$_2$); 2.16–1.91 (*m*, 3 H); 1.61–1.43 (*m*, 3 H); 1.14 (*m*, C*H*$_3$CHO); 0.81 (*t*, J = 2.3, C*H*$_3$CH$_2$). MS: 208 (6, $M^{+\cdot}$), 152 (53), 151 (11), 124 (11), 111 (14), 96 (14), 85 (16), 84 (100), 69 (20), 41 (34), 39 (13), 32 (32). Anal. calc. for $C_{13}H_{20}O_2$ (208.303): C 74.96, H 9.68; found: C 74.83, H 9.72.

6-Methyl-3-[(1-methylpropyl)oxy]-6-(2-propenyl)-2-cyclohexen-1-one (**18**). Alkylation was accomplished using a variant of the procedure above. A LDA soln. in THF (480 ml) was prepared as above from (i-Pr)$_2$NH (81 g, 0.8 mol) and 2.5M BuLi (336 ml, 0.84 mol) in hexane. After cooling to –78°, **17** was added in THF (200 ml) within 1.5 h. The resulting soln. was stirred for 45 min and HMPA (157.7 g, 0.88 mol) added *via* cannula, then a soln. of MeI (163.3 g, 0.96 mol) in THF (160 ml) was introduced dropwise. The mixture was permitted to warm to r.t. After 30 min, the starting material was completely consumed. Workup was performed as above to yield 169.4 g (95%) of **18**, after distillation. B.p. 120°/1 Torr. IR (CCl_4): 2977*s*, 2936*s*, 2880*m*, 1653*s*, 1462*m*, 1428*m*, 1374*s*, 1343*m*, 1325*m*, 1306*w*, 1264*m*, 1237*m*, 1192*s*, 1171*m*, 1119*m*, 1096*m*, 1030*w*, 995*m*, 947*w*, 914*m*. ^{1}H-NMR (300 MHz): 5.63 (*m*, C*H*=CH$_2$); 5.17 (*s*, H–C(2)); 5.00 (*s*, 1 H, CH=C*H*$_2$); 4.96 (*dd*, J = 5.0, 2.0, 1 H, CH=C*H*$_2$); 4.12 (*dd*, J = 12.2, 6.1, OCH); 2.25–2.34 (*m*, C*H*$_2$–CH=CH$_2$, H–C(4)); 2.09–2.14 (*m*, H–C(4)); 1.80–1.90 (*m*, 1 H); 1.46–1.68 (*m*, 3 H); 1.17 (*d*, J = 6.2, C*H*$_3$CHO); 1.01 (*s*, CH$_3$–C(6)); 0.84 (*t*, J = 7.4, C*H*$_3$CH$_2$). ^{13}C-NMR (300 MHz): 203.4; 174.9; 134.2; 117.7; 101.3; 75.5; 42.9; 41.4; 31.5; 28.5; 26.2; 22.0; 18.5; 9.4. MS: 222 (2, $M^{+\cdot}$), 166 (24), 152 (15), 138 (10), 85 (42), 84 (100), 69 (18), 57 (11), 43 (10), 41 (25), 39 (11), 38 (55). Anal. calc. for $C_{14}H_{22}O_2$ (222.33): C 75.63, H 9.97; found: C 75.31, H 9.84.

4-Methyl-4-(2-propenyl)-2-cyclohexen-1-one. To a soln. of **18** (25.35 g, 0.114 mol) in Et_2O (200 ml) at 0°, $LiAlH_4$ (2.16 g, 0.057 mol) was added in several portions. The mixture was allowed to warm to r.t., then cooled to 0°. A 25% aq. H_2SO_4 soln. (200 ml) was added with vigorous stirring. After 30 min, the aq. layer was extracted twice with Et_2O (250 ml). The org. layers were washed sequentially with 150-ml portions of sat. aq. Na_2CO_3 and brine, pooled, dried (K_2CO_3), and evaporated. Distillation provided 16.1 g (94%). B.p. 110°/22 Torr. Spectral data were consistent with data in [24].

4-Methyl-4-(2-propenyl)cyclohexanone (**19**). A soln. of 4-methyl-4-(2-propenyl)-2-cyclohexen-1-one (25 g, 0.16 mol) and *t*-BuOH (11.7 g, 0.158 mol) in THF (40 ml) was added to a stirred suspension of Li (4 g, 0.58 mol) in NH_3 (350 ml), maintained at –78°. After stirring for 10 min at –78°, the NH_3 was permitted to reflux for 30 min.

Subsequently, a sat. aq. NH_4Cl soln. (80 ml) was introduced. The resulting mixture was extracted thrice with 300-ml portions of Et_2O; the Et_2O extracts were washed with H_2O (150 ml) and brine (150 ml). The org. layers were dried (K_2CO_3) and evaporated. Distillation afforded 21.6 g (85%) of **19**. B.p. 94°/12 Torr. IR (CCl_4): 3413*w*, 3077*w*, 2961*s*, 2926*s*, 2857*m*, 1719*s*, 1638*m*, 1464*m*, 1445*m*, 1420*m*, 1334*m*, 1308*w*, 1231*w*, 1198*w*, 1138*m*. ^{1}H-NMR (300 MHz): 5.83 (*dtd*, J_{trans} = 8.8, J_{cis} = 7.5, 1.4, H–C(8)); 5.09 (*s*, H–C(9)); 5.04 (*d*, *J* = 8.8, H–C(9)); 2.33 (*t*, *J* = 6.8, 2 H–C(2), 2 H–C(6)); 1.76–1.58 (*m*, 2 H–C(3), 2 H–C(5)). ^{13}C-NMR (75.5 MHz): 212.24 (*s*); 134.19 (*d*); 117.63 (*t*); 44.7 (*t*); 37.44 (*t*); 36.84 (*t*); 32.43 (*s*); 23.90 (*q*). MS: 152 (4, M^c), 111 (37, $M^+ - C_3H_5$), 110 (51, $M^+ - C_3H_6$), 83 (30), 69 (35), 68 (10), 67 (18), 55 (100), 41 (53), 39 (22). Anal. calc. for $C_{10}H_{16}O$ (152.238): C 78.90, H 10.59; found: C 79.02, H 10.62.

4-Methyl-4-(2-propenyl)cyclohexanone (2,4,6-Triisopropylbenzenesulfonyl)hydrazone (**15c**). Yield 85%. M.p. 109–111°. Anal. calc. for $C_{25}H_{40}N_2O_2S$ (400.61): C 69.40, H 9.32, N 6.47, S 7.41; found: C 69.31, H 9.37, N 6.49, S 7.25.

4. Preparation of Divinylmethyl Alcohols. – 4.1. Grignard *Addition to Unsaturated Aldehydes. General Procedure.* To Mg (1.8 equiv.) and dry THF (1 ml/0.1 g Mg) under N_2, an I_2 crystal and a few drops of (*E*)-(2-bromoethenyl)trimethylsilane were added. Then, a soln. of the bromide (1.8 equiv.) in THF (8 ml/g bromide) was added dropwise. After dissolution of the Mg, the yellow-green soln. was cooled to –40°. A soln. of the unsaturated aldehyde **3** (1.0 equiv.) in THF (10 ml/g enal) was delivered dropwise. After completion of the reaction, the mixture was warmed to 0° and quenched with 4% aq. NH_4Cl soln. (20 ml/g bromide). The mixture was extracted with Et_2O (3 × 25 ml/g bromide), and the extracts were washed individually with H_2O (30 ml/g bromide) and brine (40 ml/bromide). The combined org. layers were dried (K_2CO_3), filtered, evaporated, and chromatographed.

(E)-1-(2'-Methyl-1'-cyclohexenyl)-3-(trimethylsilyl)-2-propen-1-ol (**7a**). Yield 90%. R_f 0.44 (hexane/AcOEt 4:1). IR (neat): 3349*m*, 2928*s*, 2859*m*, 2363*w*, 1734*w*, 1700*w*, 1684*w*, 1653*w*, 1617*w*, 1576*w*, 1559*w*, 1539*w*, 1522*w*, 1507*w*, 1437*w*, 1246*s*, 1194*w*, 1140*w*, 1103*w*, 1061*m*, 992*m*, 938*w*, 866*s*, 837*s*. ^{1}H-NMR (300 MHz): 6.02 (*dd*, *J* = 18.7, 4.0, H–C(2)); 5.86 (*dd*, *J* = 18.7, 1.2, H–C(3)); 5.12 (*d*, *J* = 4.1, H–C(1)); 1.99–1.55 (*m*, OH, 2 H–C(3'), 2 H–C(4'), 2 H–C(5'), 2 H–C(6')); 1.67 (*s*, CH_3); 0.07 (*s*, $(CH_3)_3Si$).

*(E)-1-(7',7'-Dimethyl-*cis*-bicyclo[4.2.0]oct-2'-en-3'-yl)-3-(trimethylsilyl)-2-propen-1-ol* (**7b**). Yield 77%. R_f 0.32 (hexane/AcOEt 5:1). IR (neat): 3545*m*, 2951*s*, 2930*s*, 2903*m*, 2860*m*, 1617*w*, 1453*m*, 1381*w*, 1368*m*, 1248*s*, 1196*w*, 1069*m*, 990*m*, 866*s*, 839*s*, 762*w*, 743*w*, 691*m*. ^{1}H-NMR (300 MHz): 6.01 (*dd*, *J* = 18.9, 4.3, H–C(2)); 5.89 (*d*, *J* = 19.0, H–C(3)); 5.68 (br. *d*, *J* = 1.9, H–C(2')); 4.48 (br. *s*, H–C(1)); 2.79 (br., H–C(1')); 2.10–1.53 (*m*, 2 H–C(8'), H–C(6'), 2 H–C(4'), 2 H–C(5'), OH); 1.19 (*s*, CH_3); 0.94 (*s*, CH_3); 0.08 (*s*, Me_3Si). MS: 264 (1, M^+), 208 (12), 135 (30), 134 (16), 127 (32), 118 (16), 117 (51), 91 (10), 79 (11), 75 (53), 73 (100), 69 (17), 57 (26), 56 (44), 55 (13), 43 (23), 42 (16), 41 (45), 39 (10). Anal. calc. for $C_{16}H_{28}OSi$: C 72.66, H 10.67; found: C 72.43, H 10.49.

(E)-1-(4',4'-Dimethyl-1',5'-cyclohexadienyl)-3-(trimethylsilyl)-2-propen-1-ol (**7c**). Yield 92%. B.p. 100°/0.05 Torr. R_f 0.27 (hexane/AcOEt 6:1). IR (neat): 3360*m*, 3020*w*, 2960*s*, 2920*m*, 2900*m*, 2860*m*, 2810*w*, 1685*m*, 1615*w*, 1470*m*, 1460 (sh), 1450*w*, 1420*m*, 1405*m*, 1375*m*, 1360*m*, 1330*w*, 1245*s*, 1200 (sh), 1190*m*, 1165*w*, 1155*w*, 1140*w*, 1120*w*, 1070*m*, 1030*m*, 990*s*, 930*w*, 870*s*, 840*s*, 760*m*, 690*m*. ^{1}H-NMR (90 MHz): 6.01–5.98 (*m*, H–C(2), H–C(3)); 5.86–5.52 (*m*, H–C(2'), H–C(5'), H–C(6')); 4.62 (br., H–C(1)); 2.19 (*d*, *J* = 4.0, 2 H–C(3')); 1.76–1.62 (br., OH); 1.08 (*s*, 2 CH_3); 0.20 (*s*, Me_3Si). MS: 236 (7, M^+), 131 (26), 107 (15), 93 (21), 91 (30), 79 (10), 77 (23), 75 (29), 73 (100), 59 (16), 45 (18), 43 (12), 41 (19), 39 (15). Anal. calc. for $C_{14}H_{24}OSi$: C 71.12, H 10.23; found: C 70.83, H 10.11.

(E)-1-(5',5'-Dimethyl-1',3'-cyclohexadienyl)-3-(trimethylsilyl)-2-propen-1-ol (**7d**). Yield 74%. B.p. 100°/0.05 Torr. R_f 0.33 (hexane/AcOEt 5:1). IR (neat): 3350*m*, 3026*w*, 2955*s*, 2864*m*, 1620*w*, 1466*w*, 1358*w*, 1248*s*, 1200*w*, 1125*w*, 1068*m*, 1024*m*, 988*m*, 864*s*, 839*s*, 729*s*, 691*w*. ^{1}H-NMR (300 MHz): 5.97 (*d*, *J* = 3.5, H–C(2), H–C(3)); 5.89–5.80 (*m*, H–C(3'), H–C(4')); 5.49 (*d*, *J* = 9.2, H–C(2')); 4.59 (br. *s*, H–C(1)); 2.00 (*s*, 2 H–C(6')); 1.65 (br., OH); 0.97 (*s*, 2 CH_3); 0.08 (*s*, $(CH_3)_3Si$). MS: 236 (8, M^+), 163 (20), 131 (36), 127 (28), 107 (11), 91 (20), 77 (12), 75 (76), 73 (100), 59 (14), 45 (16), 43 (11), 41 (11), 32 (38). HR-MS: 236.1590 ($C_{14}H_{24}OSi$, calc. 236.1596).

(E)-1-(3',4'-Dihydro-2'H-pyranyl)-3-(trimethylsilyl)-2-propen-1-ol (**7e**). Yield 82%. R_f 0.32 (hexane/AcOEt 3:1). IR (neat): 3400*m*, 2950*s*, 2930 (sh), 2900*m*, 2860*m*, 1660*m*, 1370*w*, 1245*s*, 1230*s*, 1145*s*, 1040*m*, 980*m*, 920*m*, 860*s*, 840*s*, 750*w*, 730*w*. ^{1}H-NMR (200 MHz): 6.48 (br. *s*, H–C(6')); 6.06 (*dd*, *J* = 18.1, 4.4, H–C(2)); 5.90 (*dd*, *J* = 18.1, 1.3, H–C(3)); 4.47 (*t*, *J* = 4.4, H–C(1)); 3.94 (*m*, 2 H–C(2')); 1.98 (*m*, 2 H–C(4')); 1.87 (*m*, 2 H–C(3')); 1.56 (*d*, *J* = 4.4, OH); 0.07 (*s*, Me_3Si). Compound **7e** was unstable and decomposed into **7e'**.

2-(3'-Hydroxypropyl)-5-(trimethylsilyl)-2,4-pentadienal (**7e'**). R_f 0.17 (hexane/AcOEt 3:1). IR (neat): 3400*m*, 2980*s*, 2880*m*, 2810*m*, 2710*w*, 1670*s*, 1620*m*, 1560*w*, 1440*m*, 1400*m*, 1370*m*, 1250*s*, 1150*s*, 1050*m*, 1000*m*, 985*m*, 860*s*, 840*s*, 735*m*, 695*m*. ^{1}H-NMR (200 MHz): 9.44 (*s*, CHO); 7.01 (*dd*, *J* = 17.8, 10.5, H–C(4)); 6.82 (*d*, *J* = 10.8, H–C(3)); 6.53 (*d*, *J* = 17.8, H–C(5)); 3.53 (*t*, *J* = 6.0, 2 H–C(3')); 2.50 (*t*, *J* = 7.2, 2 H–C(1')); 2.18 (br., OH); 1.70 (*m*, 2 H–C(2')); 0.15 (*s*, Me_3Si).

(E)-1-(2'-Furyl)-3-(trimethylsilyl)-2-propen-1-ol (**7f**). B.p. 90°/0.01 Torr. R_f 0.42 (hexane/AcOEt 3:1). ^{1}H-NMR (200 MHz): 7.40 (*dd*, *J* = 1.9, 0.95, H–C(5')); 6.34 (*dd*, *J* = 1.9, 1.4, H–C(4')); 6.26 (*d*, *J* = 18.7, H–C(3)); 6.23 (*dd*, *J* = 1.5, H–C(3')); 6.06 (*dd*, *J* = 18.7, 1.3, H–C(2)); 5.20 (br. *s*, H–C(1)); 2.12 (br. *s*, OH); 0.10 (*s*, Me_3Si).

(E)-1-(3'-Furyl)-3-(trimethylsilyl)-2-propen-1-ol (**7g**). B.p. 90°/0.01 Torr. R_f 0.38 (hexane/AcOEt 3:1). ^{1}H-NMR (200 MHz): 7.39 (*d*, *J* = 1.6, H–C(5')); 7.37 (*s*, H–C(2')); 6.38 (*t*, *J* = 0.95, H–C(4')); 6.22 (*dd*, *J* = 18.7, 5.1, H–C(2)); 5.98 (*dd*, *J* = 18.7, 1.0, H–C(3)); 5.15–5.14 (br. *s*, H–C(1)); 1.86 (br. *s*, OH); 0.09 (*s*, Me_3Si). IR (neat): 3349*m*, 2955*m*, 2897*m*, 2656*w*, 2350*w*, 2230*w*, 1620*m*, 1503*m*, 1408*m*, 1312*m*, 1248*s*, 1196*m*, 1159*m*, 1067*m*, 1024*s*, 992*s*, 922*w*, 868*s*, 841*s*.

(E)-Methyl 1,2,3,4-Tetrahydro-5-[1-hydroxy-3-(trimethylsilyl)-2-propenyl]pyridine-1-carboxylate (**7h**). IR (CCl_4): 2956*s*, 2898*m*, 1711*vs*, 1621*m*, 1577*w*, 1560*w*, 1539*w*, 1517*w*, 1446*s*, 1401*s*, 1373*s*, 1346*m*, 1320*s*, 1249*s*, 1193*s*, 1179*s*, 1156*s*, 1120*m*, 1077*m*, 1048*m*. ^{1}H-NMR (300 MHz): 6.96–6.84 (*m*, H–C(2)); 6.05–5.85 (*m*, H–C(2'), H–C(3')); 4.57–4.48 (*m*, H–C(1')); 3.7–3.4 (*m*, 2 H–C(6)); 3.72 (*s*, CH_3O); 2.04–1.74 (*m*, 2 H–C(4), 2 H–C(5)); 0.04 (*s*, Me_3Si).

4.2. *Vinyllithium Addition to β-Silyl Enals. Shapiro Reaction. General Procedure.* To the hydrazone **15** (1.01 g, 2.48 mmol) in hexane and *N,N,N',N'*-tetramethylethylenediamine (TMEDA; 10 ml/g hydrazone) at −78°, *s*-BuLi (2.2 equiv.) was added dropwise, the red soln. stirred for 2.5 h, and warmed to 0° for 10 min. The resulting yellow soln. was cooled to −50° and the β-silyl enal **6** (1 equiv.) was added in hexane. After warming to 0°, the mixture was quenched with H_2O (10 ml/g hydrazone). The mixture was extracted with Et_2O (3 × 20 ml/g hydrazone). The org. layers were washed with H_2O (5 × 20 ml/g hydrazone) until the aq. layer was neutral to litmus. The org. layers were dried (K_2CO_3), filtered, evaporated, and chromatographed on silica gel. Anal. data were obtained from a distilled sample.

(E)-1-(4',4'-Dimethyl-1'-cyclohexenyl)-3-(trimethylsilyl)-2-propen-1-ol (**7k**). Yield 78%. B.p. 95°/0.05 Torr. R_f 0.34 (hexane/AcOEt 5:1). IR (neat): 3340*m*, 2950*s*, 2900*s*, 2865*s*, 2845*m*, 2830*m*, 1610*m*, 1460 (sh), 1450*m*, 1430*m*, 1380*m*, 1360*m*, 1245*s*, 1210*m*, 1165*m*, 1130*m*, 1070*m*, 1050 (sh), 980*s*, 920*m*, 865*s*, 835*s*, 750*m*, 730*m*, 690*m*. ^{1}H-NMR (360 MHz): 6.01 (*dd*, *J* = 18.8, 4.8, H–C(2)); 5.89 (*dd*, *J* = 18.9, 0.8, H–C(3)); 5.63 (br. *d*, *J* = 4.5, H–C(2')); 4.49 (*d*, *J* = 4.4, H–C(1)); 1.99–1.83 (*m*, 2 H–C(3'), 2 H–C(6')); 1.63 (br. *s*, OH); 1.37 (*t*, *J* = 6.4, 2 H–C(5')); 0.90 (*s*, CH_3); 0.88 (*s*, CH_3); 0.07 (*s*, Me_3Si). MS: 238 (4, $M^{+\cdot}$), 237 (4), 133 (22), 105 (13), 95 (10), 92 (25), 91 (32), 79 (11), 75 (62), 73 (100), 59 (15), 45 (12), 41 (13). Anal. calc. for $C_{14}H_{26}OSi$: C 70.50, H 11.01; found: C 70.20, H 11.32.

1-(1'-Cyclohexenyl)-3-(trimethylsilyl)-2-buten-1-ol (**7i**). A soln. of **6b** in hexane was added to the anion derived from cyclohexanone trisylhydrazone. Yield 71%. R_f 0.45, 0.41 (2 geometrical isomers, hexane/AcOEt 4:1). IR (CCl_4): 3615*m*, 3470*w*, 2934*s*, 2861*m*, 2840*m*, 1619*w*, 1439*m*, 1368*w*, 1248*s*, 1136*m*, 1051*w*, 995*m*, 947*w*, 918*m*. ^{1}H-NMR (200 MHz): 5.74 (*d*, *J* = 1.9, H–C(2)); 5.69–5.67 (*m*, H–C(2')); 4.84 (*d*, *J* = 7.6, H–C(1)); 2.04–1.96 (*m*, 2 H–C(3'), 2 H–C(6')); 1.73 (*d*, *J* = 1.9, CH_3); 1.62–1.51 (*m*, 2 H–C(4'), 2 H–C(5')); 0.06 (*s*, Me_3Si). MS: 224 (2, $M^{+\cdot}$), 119 (11), 91 (15), 75 (43), 73 (100, Me_3Si), 67 (12), 45 (14), 41 (11). Anal. calc. for $C_{13}H_{24}OSi$: C 69.58, H 10.78, Si 12.51; found: C 69.57, H 10.63, Si 12.49.

1-(1'-Cyclohexenyl)-2-[(trimethylsilyl)methylidene]-4-penten-1-ol (**7j**). The analogous procedure to that for **7i** was used employing **6c**. Yield 47%. R_f 0.49 (hexane/AcOEt 4:1). IR (CCl_4): 3619*m*, 3081*w*, 2936*s*, 2859*m*, 2840*w*, 1617*m*, 1437*m*, 1248*s*, 1213*w*, 1138*m*, 1078*w*, 1049*w*, 1024*m*, 994*m*, 916*s*. ^{1}H-NMR (200 MHz): 5.83–5.68 (*m*, SiCH=C, H–C(4), H–C(2')); 5.05 (*dd*, *J* = 7.6, 1.6, 1 H–C(5)); 4.99 (br. *s*, 1 H–C(5)); 4.44 (br. *s*, H–C(1)); 2.90, 2.78 (2*dd*, *J* = 14.6, 7.0, 2 H–C(3)); 2.05–1.74 (*m*, 2 H–C(3'), 2 H–C(6')); 1.66–1.48 (br. *s*, 2 H–C(4'), 2 H–C(5'), OH); 0.14 (*s*, Me_3Si). MS: 250 (0.4, $M^{+\cdot}$), 75 (29), 74 (9), 73 (100, Me_3Si), 45 (10). Anal. calc. for $C_{15}H_{26}OSi$: C 71.93, H 10.46, Si 11.21; found: C 71.70, H 10.19, Si 11.15.

(E)-1-[4'-methyl-4'-(2''-propenyl)-1'-cyclohexenyl]-3-(trimethylsilyl)-2-propen-1-ol (**7l**). Yield 92%. R_f 0.44 (hexene/AcOEt 4:1). IR (neat): 3351*m*, 3075*w*, 2955*s*, 2913*s*, 1671*w*, 1638*w*, 1617*m*, 1559*w*, 1507*w*, 1435*m*, 1375*m*, 1302*m*, 1248*s*, 1200*w*, 1123*w*, 1071*m*, 992*s*, 912*m*, 868*s*, 839*s*. ^{1}H-NMR (300 MHz): 6.04 (*dd*, *J* = 18.9, 4.4, H–C(2)); 5.86 (*d*, *J* = 19.2, H–C(3)); 5.96–5.76 (*m*, *HC*=CH_2); 5.62 (br. *s*, H–C(2')); 5.02–4.94 (*m*, HC=CH_2); 4.46 (*d*, *J* = 4.4, H–C(1)); 2.02–1.76 (*m*, 8 H); 1.38 (*dd*, *J* = 12.4, 6.3, 2 H); 0.86, 0.84 (2*s*, CH_3, 2 diastereoisomers, 3 H); 0.05 (*s*, 9 H).

(E)-1-[4'-(3''-Hydroxypropyl)-4'-methyl-1'-cyclohexenyl]-3-(trimethylsilyl)-2-propen-1-ol (**20**). To a soln. of **7l** (12.31 g, 46.5 mmol) in THF (45 ml) at 0° was added an excess (214 ml, 107 mmol) of 9-borabicyclo[3.3.1]nonane (9-BBN) and the resulting soln. stirred for 2 h at r.t. The mixture was then cooled to 0°; H_2O (12.3 ml) and 3N aq. NaOH (52 ml) were added. Subsequently, 30% H_2O_2 (52 ml) was slowly added with cooling; the soln. was maintained at or below r.t. The mixture was stirred for 1 h, then saturated with solid NaCl and extracted with Et_2O (3 × 300 ml). The Et_2O extracts were washed with brine and dried (K_2CO_3). After concentration, the residue was chromatographed using Et_2O as eluent to afford 10.7 g (81%) of **20**. R_f 0.21 (hexane/AcOEt 1:1). IR (neat): 3854*w*,

3386*s*, 2953*s*, 2361*w*, 2245*w*, 1711*w*, 1653*w*, 1617*m*, 1559*w*, 1507*w*, 1435*m*, 1377*m*, 1306*m*, 1248*s*, 1127*m*, 1059*s*, 990*m*, 909*s*, 866*s*, 839*s*. ^{1}H-NMR (300 MHz): 5.98 (*dd*, *J* = 18.9, 4.3, H–C(2)); 5.88 (*d*, *J* = 18.9, H–C(3)); 5.63 (br. *s*, H–C(2')); 4.48 (br. *s*, H–C(1)); 3.61 (*t*, *J* = 6.4, C*H*$_2$OH); 2.17–1.18 (*m*, 11 H); 0.87, 0.85 (2*s*, total 3 H, CH$_3$–C(4')); 0.07 (*s*, Me$_3$Si).

(E)-1-(3',4'-Dihydro-2'H-pyran-6'yl)-3-(trimethylsilyl)-2-propen-1-ol (**7n**). The metallation of dihydropyran was accomplished according to [11]. A mixture of 3,4-dihydro-2*H*-pyran (1.036 g, 12.3 mmol) and dry THF (0.6 ml, 7.4 mmol) under N_2 was cooled to –78° and treated with *t*-BuLi (13.3 ml of a 1.02M soln. in pentane, 13.5 mmol). The soln. was warmed to –5°, stirred for 30 min, and treated with THF (0.5 ml). The mixture was cooled to –78° and **6a** (1.74 g, 13.5 mmol) was added. The mixture was allowed to warm to 0°, quenched with H_2O (50 ml) and extracted with Et_2O (3 × 200 ml). The org. layers were washed with H_2O (2 × 150 ml) and brine (150 ml), dried (K_2CO_3), evaporated, and chromatographed to afford 2.015 g (77%) of **7n**. B.p. 100°/0.05 Torr. R_f 0.33 (hexane/AcOEt 4:1). IR (neat): 3411*m*, 2954*s*, 2897*m*, 2850*m*, 1741*w*, 1675*m*, 1619*m*, 1466*m*, 1448*w*, 1436*w*, 1389*m*, 1350*m*, 1247*s*, 1232*s*, 1191*m*, 1154*m*, 1117*m*, 1088*s*, 1064*s*, 992*s*, 917*m*, 867*s*, 838*s*, 770*m*, 750*m*, 732*m*, 693*m*. ^{1}H-NMR (200 MHz): 6.10 (*dd*, *J* = 18.7, 4.4, H–C(2)); 5.97 (*dd*, *J* = 18.7, 1.3, H–C(3)); 4.75 (*t*, *J* = 3.8, H–C(5')); 4.42 (*t*, *J* = 5.0, H–C(1')); 4.02 (*m*, 2 H–C(2')); 2.09 (*d*, *J* = 5.7, OH); 2.05–2.00 (*m*, 2 H–C(4')); 1.87–1.76 (*m*, 2 H–C(3')); 0.07 (*s*, Me$_3$Si). MS: 212 (12, M^+), 168 (11), 167 (11), 114 (47), 94 (10), 77 (10), 75 (91), 73 (100), 59 (13), 55 (11), 45 (15), 43 (12). Anal. calc. for $C_{11}H_{20}O_2Si$: C 62.22, H 9.49; found: C 61.84, H 9.65.

(E)-1-[6'-(Benzyloxy)-1'-cyclohexenyl]-3-(trimethylsilyl)-2-propen-1-ol (**7p**). The metal-halogen exchange was done according to [25]. A soln. of *1-(benzyloxy)-2-bromo-2-cyclohexene* (**26**; 0.118 g, 0.442 mmol) in THF (5 ml) was cooled to –78° and treated with *t*-BuLi (0.55 ml of a 1.62M soln. in pentane, 0.892 mmol). After stirring for 1 h, **6a** (0.062 g, 0.486 mmol) in THF (2 ml) was added. The mixture was allowed to warm to 0° and quenched with 4% NH_4Cl soln. (5 ml). The mixture was extracted with Et_2O (3 × 10 ml), the org. layers were washed with brine (3 × 10 ml), dried (K_2CO_3), filtered, evaporated, and chromatographed to afford 0.097 g (69%) of **7p**. B.p. 145°/0.05 Torr. R_f 0.25 (hexane/AcOEt 5:1). IR (neat): 3410*m*, 3070*w*, 3030*w*, 3015*w*, 2930*s*, 2900 (sh), 2850*s*, 2820*m*, 1610*w*, 1495*w*, 1450*m*, 1435*m*, 1350*m*, 1330*m*, 1300*m*, 1245*s*, 1200*w*, 1160*w*, 1130*w*, 1085*m*, 1060*s*, 1020*m*, 985*m*, 960*w*, 940*w*, 920*m*, 865*s*, 840*s*, 810 (sh), 730*s*, 695*s*. ^{1}H-NMR (360 MHz): 7.39–7.30 (*m*, Ph); 6.01 (*dd*, *J* = 18.6, 5.5, H–C(2)); 5.94 (*t*, *J* = 3.7, H–C(2')); 5.85 (br. *d*, *J* = 19.2, H–C(3)); 4.71 (*d*, *J* = 11.4, H–C(7')); 4.66 (br. *d*, *J* = 4.7, H–C(1)); 4.47 (*d*, *J* = 11.6, H–C(7')); 3.99 (*t*, *J* = 3.5, H–C(6')); 2.88 (*d*, *J* = 2.0, OH); 2.16–1.59 (*m*, 6 H); 0.09 (*s*, Me$_3$Si). MS: 225 (1, M^+ – PhCH$_2$), 208 (13), 207 (10), 135 (14), 118 (27), 117 (14), 107 (23), 92 (17), 91 (100), 79 (18), 75 (41), 73 (93). Anal. calc. for $C_{19}H_{28}O_2Si$: C 72.10, H 8.91; found: C 72.07, H 8.88.

(E)-1-[2'-(Benzyloxymethyl)-1'-cyclohexenyl]-3-(trimethylsilyl)-2-propen-1-ol (**7q**). Prepared from **24** analogously to **7p**. Yield 1.172 g (65%). R_f 0.26 (hexane/AcOEt 5:1). IR (neat): 3416*m*, 3030*w*, 2930*s*, 2859*m*, 1617*w*, 1497*w*, 1455*w*, 1364*s*, 1201*w*, 1134*w*, 1069*m*, 1028*w*, 994*m*, 939*w*, 866*s*, 837*s*, 750*m*, 735*m*, 696*m*. ^{1}H-NMR (300 MHz): 7.35–7.25 (*m*, Ph); 6.02 (*dd*, *J* = 18.9, 3.9, H–C(2)); 5.89 (*dd*, *J* = 18.9, 1.1, H–C(3)); 5.02 (br., H–C(1)); 4.48 (*ABq*, *J* = 11.8, 2 H–C(8')); 4.01 (*ABq*, *J* = 10.9, 2 H–C(7')); 2.21 (*d*, *J* = 3.5, OH); 2.14–1.92 (*m*, 2 H–C(3'), 2 H–C(6')); 1.59 (*m*, 2 H–C(4'), 2 H–C(5')); 0.06 (*s*, Me$_3$Si). ^{13}C-NMR (75.5 MHz): 146.1 (C(3)); 138.2 (C(9')); 137.3 (C(2')); 131.0 (C(1')); 128.8 (C(2)); 128.4 (C(10')); 127.8 (C(11')); 127.7 (C(12')); 72.8 (C(1)); 72.4 (C(8')); 69.9 (C(7')); 29.3; 24.1; 22.6; 22.56; –1.2 (Me$_3$Si). MS: 149 (28), 148 (14), 132 (20), 107 (14), 104 (41), 92 (12), 91 (100), 79 (11), 75 (29), 73 (97), 67 (12), 45 (11), 43 (22), 32 (39), 31 (56). Anal. calc. for $C_{20}H_{30}O_2Si$: C 72.67, H 9.15; found: C 72.81, H 9.22.

5. Divinyl-Ketone Synthesis. – 5.1. *General Procedure with Nickel Peroxide (Method A).* A magnetically stirred soln. of the alcohol **7** in dry Et_2O (0.1M) was cooled to 0° and treated with 1.5–1.8 equiv. of nickel peroxide in one portion. The mixture was warmed to r.t. after 30 min and the progress monitored by TLC (*ca.* 2 h). The nickel peroxide was filtered (*Celite*) and washed 3 times with acetone. Evaporation of the filtrate afforded the crude ketone which was generally distilled directly. Cases in which chromatography was necessary are indicated by R_f data.

5.2. *General Procedure using $BaMnO_4$ (Method B).* A stirred soln. of the alcohol **7** in dry CH_2Cl_2 (0.1M) was cooled to 0° and treated with 10 equiv. of $BaMnO_4$. The mixture was warmed to r.t. and monitored by TLC. Upon completion (usually *ca.* 12 h), the mixture was filtered through *Celite*, and the solids were washed with CH_2Cl_2. The filtrate was concentrated, chromatographed, and distilled.

(E)-1-(2'-Methyl-1'-cyclohexenyl)-3-(trimethylsilyl)-2-propen-1-one (**1a**). *Method B.* Yield 85%. B.p. 90°/0.1 Torr. R_f 0.63 (hexane/AcOEt 4:1). IR (CCl_4): 2936*s*, 2861*m*, 1653*s*, 1584*m*, 1439*m*, 1379*w*, 1360*w*, 1279*m*, 1250*s*, 1237*m*, 1225*m*, 1175*m*, 1140*w*, 1109*w*, 1069*w*, 999*s*, 866*s*, 804*s*. ^{1}H-NMR (300 MHz): 7.02 (*d*, *J* = 19.1, H–C(2)); 6.57 (*d*, *J* = 19.1, H–C(3)); 2.16 (br. *t*, *J* = 1.8, 2 H); 2.06 (br. *s*, 2 H); 1.67 (*s*, CH$_3$); 1.67–1.63 (*m*, 2 H–C(4'), 2 H–C(5')); 0.14 (*s*, Me$_3$Si). MS: 222 (0.47, M^+), 207 (5), 149 (66), 148 (26), 132 (18), 131 (12), 123 (60), 120 (12), 117

(18), 107 (45), 105 (11), 104 (79), 95 (100), 91 (37), 79 (10), 75 (30), 73 (70), 67 (36), 59 (12), 55 (22), 53 (13), 45 (23), 41 (23), 39 (11). Anal. calc. for $C_{13}H_{22}OSi$: C 70.21, H 9.97; found: C 70.41, H 10.07.

*(E)-1-(7',7'-Dimethyl-*cis*-bicyclo[4.2.0]oct-2'-en-3'-yl)-3-(trimethylsilyl)-2-propen-1-one* (**1b**). *Method B.* Yield 83%. B.p. 95°/0.05 Torr. R_f 0.37 (hexane/AcOEt 10:1). IR (neat): 3050*w*, 2951*s*, 2943*s*, 2901*m*, 2863*m*, 1651*s*, 1624*m*, 1586*w*, 1455*w*, 1377*m*, 1250*s*, 1217*m*, 1194*w*, 1148*w*, 1011*w*, 993*m*, 974*w*, 872*s*, 845*s*, 750*m*, 696*w*. ^{1}H-NMR (300 MHz): 7.09 (*d*, *J* = 18.5, H–C(2)); 7.04 (*d*, *J* = 18.8, H–C(3)); 6.90 (*dd*, *J* = 3.8, 2.1, H–C(2')); 3.02 (*m*, H–C(1')); 2.62 (*dt*, *J* = 16.6, 3.9, H–C(4')); 2.04–1.76 (*m*, 1 H–C(8'), 1 H–C(5'), H–C(6'), H–C(4')); 1.72 (*t*, *J* = 10.1, 1 H–C(8')); 1.53 (*m*, 1 H–C(5')); 1.23 (*s*, CH_3); 0.96 (*s*, CH_3); 0.14 (*s*, Me_3Si). ^{13}C-NMR (75.5 MHz): 190.2 (C(1)); 146.2 (C(3)); 143.9 (C(2')); 140.5 (C(3')); 137.2 (C(2)); 42.4 (C(6')); 40.5 (C(8')); 34.4 (C(7')); 29.8 (C(1')); 29.5 (CH_3); 24.1 (CH_3); 22.6 (C(5')); 21.3 (C(4')); –1.7 (Me_3Si). MS: 262 (2, M^+), 206 (15), 191 (12), 190 (14), 189 (35), 133 (13), 116 (26), 115 (11), 107 (21), 79 (10), 77 (13), 75 (44), 73 (100), 69 (11), 45 (12), 41 (17). Anal. calc. for $C_{16}H_{26}OSi$: C 73.22, H 9.99; found: C 73.19, H 10.10.

(E)-1-(4',4'-Dimethyl-1',5'-cyclohexadienyl)-3-(trimethylsilyl)-2-propen-1-one (**1c**). *Method B.* Yield 86%. B.p. 110°/0.04 Torr. R_f 0.34 (hexane/AcOEt 8:1). IR (neat): 3040*w*, 3010*w*, 2960*s*, 2930*m*, 2905*m*, 2870*m*, 2800*w*, 1655*s*, 1590*s*, 1470*m*, 1460 (sh), 1450*m*, 1420*m*, 1405*m*, 1380*w*, 1360*m*, 1345*m*, 1250*s*, 1230 (sh), 1190*m*, 1170*m*, 1160*m*, 1120*m*, 1045*m*, 1015*m*, 990*s*, 975*m*, 940*m*, 905 (sh), 870*s*, 850*s*, 750*s*, 720*w*, 700*m*, 670*m*. ^{1}H-NMR (360 MHz): 7.17 (*d*, *J* = 18.6, H–C(2)); 7.04 (*d*, *J* = 18.6, H–C(3)); 6.83 (*t*, *J* = 4.5, H–C(2')); 6.40 (*dd*, *J* = 9.8, 1.5, H–C(6')); 5.71 (*d*, *J* = 9.8, H–C(5')); 2.34 (*d*, *J* = 4.7, 2 H–C(3')); 1.03 (*s*, 2 CH_3); 0.16 (*s*, Me_3Si). MS: 234 (9, M^+), 219 (26), 203 (17), 135 (10), 129 (11), 127 (12), 107 (10), 91 (16), 75 (44), 73 (100), 45 (12). Anal. calc. for $C_{14}H_{22}OSi$: C 71.73, H 9.46; found: C 71.40, H 9.81.

(E)-1-(5',5'-Dimethyl-1',3'-cyclohexadienyl)-3-(trimethylsilyl)-2-propen-1-one (**1d**). *Method B.* Yield 80%. B.p. 100°/0.07 Torr. M.p. 37–38°. R_f 0.27 (hexane/AcOEt 12:1). IR (CCl_4): 3030*w*, 2960*m*, 2870*w*, 1645*s*, 1588*w*, 1564*m*, 1468*w*, 1402*w*, 1381*w*, 1360*w*, 1252*s*, 1231*m*, 1155*m*, 991*m*, 876*m*, 864*m*, 847*m*. ^{1}H-NMR (300 MHz): 7.14 (*d*, *J* = 18.6, H–C(2)); 7.10 (*d*, *J* = 18.6, H–C(3)); 6.97 (*d*, *J* = 3.5, H–C(2')); 6.00 (*m*, H–C(3'), H–C(4')); 2.44 (*s*, 2 H–C(6')); 1.03 (*s*, 2 CH_3); 0.16 (*s*, Me_3Si). MS: 234 (4, M^+), 219 (24), 203 (33), 135 (19), 129 (15), 127 (10), 107 (18), 91 (27), 75 (69), 73 (100), 45 (13). Anal. calc. for $C_{14}H_{22}OSi$: C 71.73, H 9.46; found: C 71.95, H 9.63.

*(E)-1-(3',4'-Dihydro-2'*H*-pyran-5'-yl)-3-(trimethylsilyl)-2-propen-1-one* (**1e**). *Method B.* Yield 80%. B.p. 75°/0.05 Torr. R_f 0.30 (hexane/AcOEt 4:1). IR ($CHCl_3$): 3020*w*, 3010*m*, 2960*m*, 2900*w*, 2880*w*, 2850*w*, 1660 (sh), 1620*s*, 1585*s*, 1465*w*, 1445*w*, 1435*w*, 1400*m*, 1330*m*, 1315*m*, 1280*m*, 1265*s*, 1255 (sh), 1180*s*, 1085*w*, 1050*w*, 1015*s*, 990*m*, 975*w*, 885*m*, 870*s*, 860 (sh), 845*s*, 830*m*. ^{1}H-NMR (360 MHz): 7.70 (br. *s*, H–C(6')); 7.05 (*d*, *J* = 18.6, H–C(2)); 6.83 (*d*, *J* = 18.6, H–C(3)); 4.10 (*t*, *J* = 5.2, 2 H–C(2')); 2.34 (*t*, *J* = 6.2, 2 H–C(4')); 1.93–1.87 (*m*, 2 H–C(3')); 0.14 (*s*, Me_3Si). MS: 210 (11, M^+), 195 (13), 167 (16), 111 (100), 83 (32), 75 (23), 73 (58), 55 (19), 45 (19), 43 (19), 39 (10). Anal. calc. for $C_{11}H_{18}O_2Si$: C 62.81, H 8.63; found: C 62.66, H 8.58.

(E)-1-(2'-Furyl)-3-(trimethylsilyl)-2-propen-1-one (**1f**). *Method A.* Yield 92%. IR ($CHCl_3$): 2960*s*, 1650v*s*, 1590*s*, 1465*s*, 1392*s*, 1270–1190*s*, 1160*m*, 1085*m*, 1034*s*, 995*s*, 924*m*, 912*m*. ^{1}H-NMR (200 MHz): 7.59 (*d*, *J* = 0.6, 1 H); 7.40 (*d*, *J* = 18.7, 1 H); 7.24 (*d*, *J* = 3.5, 1 H); 7.15 (*d*, *J* = 18.7, 1 H); 6.53–6.50 (*m*, 1 H); 0.13 (*s*, 9 H). MS: 194 (11, M^+), 193 (16, $M^+ - H$), 179 (100, $M^+ - Me$), 125 (14), 105 (20), 99 (12), 95 (75, $M^+ - CHCHSiMe_3$), 91 (11), 83 (10), 77 (11), 75 (20), 73 (69), 45 (25), 43 (30), 39 (27). Anal. calc. for $C_{10}H_{14}O_2Si$: C 61.81, H 7.26; found: C 61.47, H 7.32.

(E)-1-(3'-Furyl)-3-(trimethylsilyl)-2-propen-1-one (**1g**). *Method A.* Yield 98%. IR ($CHCl_3$): 2960*m*, 1650*s*, 1585*s*, 1505*s*, 1388*m*, 1318*s*, 1292*s*, 1250–1190*s*, 1155*s*, 1045*s*, 987*s*, 946*s*. ^{1}H-NMR (200 MHz): 8.12 (*s*, 1 H); 7.49 (*s*, 1 H); 7.34 (*d*, *J* = 18.9); 6.96 (*d*, *J* = 18.9, 1 H); 6.88 (*s*, 1 H); 0.21 (*s*, 9 H). MS: 194 (18, M^+), 181 (15), 180 (47), 179 (100, $M^+ - Me$), 165 (12), 161 (10), 151 (45), 149 (11), 125 (35), 111 (13), 105 (15), 96 (10), 95 (100, $M^+ - CHCHSiMe_3$), 91 (11), 83 (14), 75 (23), 74 (12), 73 (100, MeSi), 67 (11), 59 (13), 58 (12), 45 (28), 43 (31), 39 (39). Anal. calc. for $C_{10}H_{14}O_2Si$: C 61.81, H 7.26; found: C 61.59, H 7.54.

(E)-Methyl 3-[1-Oxo-3-(trimethylsilyl)-2-propenyl]-1,2,3,4-tetrahydropyridine-1-carboxylate (**1h**). *Method A.* Yield 61%. R_f 0.20 (hexane/AcOEt 4:1). IR ($CHCl_3$): 3500*w* (br.), 3010*m*, 2968*s*, 2902*m*, 2870*w*, 1722*s* (br.), 1618*s*, 1575*s*, 1449*s*, 1391*s*, 1385*s*, 1368*m*, 1351*m*, 1305*s*, 1250–1178*s* (br.), 1120*m*, 1080*w*, 1060*m*, 983*s*. ^{1}H-NMR (200 MHz): 8.08 (br. *s*, H–C(6)); 6.98 (br. *s*, H–C(2'), H–C(3')); 3.79 (*s*, MeO); 3.58 (*t*, *J* = 5.7, 2 H–C(2)); 2.31 (*t*, *J* = 6.0, 2 H–C(4)); 1.85 (*m*, H–C(3)); 0.09 (*s*, Me_3Si). MS: 267 (25, M^+), 258 (38, $M^+ - Me$), 194 (26, $M^+ - Me_3Si$), 168 (100, $M^+ - CHCHSiMe_3$), 73 (18, Me_3Si). Anal. calc. for $C_{13}H_{21}NO_3Si$: C 58.3, H 7.92, N 5.24; found: C 58.32, H 7.96, N 5.21.

1-(1'-Cyclohexenyl)-3-(trimethylsilyl)-2-buten-1-one (**1i**). *Method A.* Yield 55% (12 h). B.p. 100°/0.03 Torr. R_f 0.62 (hexane/AcOEt 4:1). IR (CCl_4): 2942*s*, 2863*m*, 1647*vs*, 1578*w*, 1435*m*, 1385*w*, 1269*m*, 1250*s*, 1210*s*, 1136*w*, 1017*w*, 968*w*, 914*w*. ^{1}H-NMR (200 MHz): (*E*)-isomer: 6.86–6.81 (*m*, H–C(2')); 6.63 (*d*, *J* = 1.6, H–C(2));

2.28–2.16 (*m*, 2 H–C(4'), 2 H–C(6')); 2.25 (*d*, J = 1.6, CH_3); 1.64–1.55 (*m*, 2 H–C(3'), 2 H–C(6'); 0.11 (*s*, Me_3Si); (*Z*)-isomer: 7.07 (*d*, J = 1.6, H–C(2)); 6.92 (*m*, H–C(2')); 2.28–2.16 (*m*, 2 H–C(4'), 2 H–C(5')); 2.27 (*d*, J = 1.6, CH_3); 1.64–1.55 (*m*, 2 H–C(3'), 2 H–C(6')); 0.13 (*s*, Me_3Si). MS: 222 (4, M^+), 207 (39, M^+ – Me), 104 (14), 91 (12), 81 (12), 75 (41), 73 (100, Me_3Si), 46 (18), 41 (12). Anal. calc. for $C_{13}H_{22}OSi$: C 70.21, H 9.97; Si 12.63; found: C 70.44, H 10.00, Si 12.59.

1-(1'-Cyclohexenyl)-2-[(trimethylsilyl)methylidene]-4-penten-1-one (**1j**). *Method A.* Yield 44% (24 h). IR (CCl_4): 3081*w*, 2942*m*, 2863*w*, 1638*s*, 1595*w*, 1449*w*, 1435*w*, 1377*w*, 1250*s*, 1213*m*, 1136*w*, 1065*w*, 994*w*, 976*w*, 912*m*, 895*m*. ^{1}H-NMR (200 MHz): 6.62–6.59 (*m*, H–C(2')); 5.95 (*s*, SiCH=C); 5.8–5.6 (*m*, CH=CH_2); 5.07–4.94 (*m*, CH=CH_2); 3.23–3.18 (*m*, CH_2–CH=CH_2); 2.28–2.22 (*m*, 2 H–C(3'), 2 H–C(6')); 1.68–1.59 (*m*, 2 H–C(4'), 2 H–C(5')); 0.19 (*s*, Me_3Si). MS: 248 (8, M^+), 233 (11, M^+ – Me), 81 (10), 75 (20), 73 (100, Me_3Si), 45 (11). Anal. calc. for $C_{15}H_{24}OSi$: C 72.52, H 9.74, Si 11.30; found: C 72.44, H 9.71, Si 11.24.

(E)-1-(4',4'-Dimethyl-1'-cyclohexenyl)-3-(trimethylsilyl)-2-propen-1-one (**1k**). *Method A.* Yield 69%. B.p. 65°/0.05 Torr. R_f 0.32 (hexane/AcOEt 12:1). IR (neat): 3035*w*, 2950*s*, 2920*s*, 2860*s*, 2820*w*, 1640*s*, 1585*m*, 1450*m*, 1430*m*, 1420*m*, 1380*s*, 1360*m*, 1350*w*, 1325*m*, 1295*w*, 1245*s*, 1235*s*, 1210*m*, 1190*m*, 1160*s*, 1150*m*, 1125*m*, 1050*m*, 1030*m*, 990*s*, 960*m*, 940*m*, 930*m*, 865*s*, 840*s*, 800*w*, 765*m*, 745*s*, 710*w*, 695*m*, 640*m*, 605*m*. ^{1}H-NMR (360 MHz): 7.10 (*d*, J = 18.6, H–C(2)); 7.07 (*d*, J = 18.6, H–C(3)); 6.89 (*m*, H–C(2')); 2.35 (*m*, 2 H); 2.06 (br. *s*, 2 H); 1.42 (*t*, J = 6.5, 2 H–C(5')); 0.93 (*s*, 2 CH_3); 0.14 (*s*, Me_3Si). MS: 236 (13, M^+), 221 (18), 180 (10), 165 (29), 163 (14), 146 (15), 137 (26), 131 (20), 127 (10), 91 (10), 81 (19), 75 (50), 73 (100), 69 (14), 67 (11), 59 (12), 53 (19), 45 (17), 43 (14), 41 (21). Anal. calc. for $C_{14}H_{24}OSi$: C 71.13, H 10.22; found: C 70.93, H 10.03.

(E)-1-[4'-(3''-Hydroxypropyl)-4'-methyl)-1'-cyclohexenyl]-3-(trimethylsilyl)-2-propen-1-one (**21**). *Method B.* Yield 88%. R_f 0.35 (hexane/AcOEt 1:1). IR (CCl_4): 3631*w*, 3449*w*, 2957*s*, 1653*s*, 1588*w*, 1456*w*, 1420*w*, 1385*w*, 1250*s*, 1237*s*, 1146*w*, 1057*m*. ^{1}H-NMR (300 MHz): 7.06 (*d*, J = 18.8, H–C(2) or H–C(3)); 7.01 (*d*, J = 18.8, H–C(2) or H–C(3)); 6.85 (*t*, J = 3.4, H–C(2')); 3.56 (*t*, J = 6.6, CH_2OH); 2.33–2.24 (*m*, 2 H–C(6'), OH); 2.04 (*t*, $J \approx$ 2.8, H–C(3')); 2.01 (*t*, $J \approx$ 2.8, H–C(3')); 1.55–1.46 (*m*, CH_2CH_2–C(4')); 1.40 (*t*, J = 6.4, CH_2CH_2–C(4')); 1.27–1.18 (*m*, 2 H–C(5')); 0.84 (*s*, CH_3); 0.09 (*s*, Me_3Si). ^{13}C-NMR (75.5 MHz): 190.36; 146.38; 139.94; 138.41; 136.90; 63.28; 38.76; 36.99; 32.65; 30.61; 26.72; 24.33; 20.79; –1.85. MS: 280 (6, M^+), 221 (16), 205 (28), 165 (12), 131 (19), 107 (13), 95 (39), 93 (18), 91 (15), 85 (10), 82 (19), 81 (37), 79 (20), 77 (13), 75 (61), 73 (100, Me_3Si), 71 (16), 69 (21), 68 (22), 67 (43), 57 (41), 56 (18), 55 (41), 54 (14), 53 (18), 45 (14), 44 (11), 43 (19), 41 (48). Anal. calc. for $C_{16}H_{28}O_2Si$ (280.486): C 68.52, H 10.06; found: C 68.66, H 9.99.

(E)-3-{1'-Methyl-4'-[1''-oxo-3''-(trimethylsilyl)-2''-propenyl]-3'-cyclohexenyl}propyl Trichloroacetate (**1m**). To a soln. of **21** (9 g, 32.1 mmol) in CH_2Cl_2 (170 ml) at 0°, 4-(dimethylamino)pyridine (0.39 g, 3.2 mmol), pyridine (4.2 ml, 51.3 mmol), and trichloroacetyl chloride (4.3 ml, 38.5 mmol) were added at 0°. TLC showed the reaction was complete immediately. The mixture was added to brine (250 ml) and extracted thrice with Et_2O (425 ml). The individual org. extracts were washed with H_2O (2 × 250 ml) and brine (1 × 250 ml). The org. phases were dried (K_2CO_3), evaporated, and chromatographed (hexane/AcOEt 10:1): 11.90 g (87%) of **1m**. M.p. 45–47°. R_f 0.51 (hexane/AcOEt 4:1). IR (CCl_4): 2959*m*, 2926*m*, 1769*s*, 1653*s*, 1588*w*, 1453*w*, 1386*m*, 1237*s*, 1157*w*, 1017*w*. ^{1}H-NMR (300 MHz): 7.12 (*d*, J = 18.8, 1 H); 7.02 (*d*, J = 18.8, 1 H); 6.87 (br. *s*, H–C(3')); 4.35 (*t*, J = 6.51, CH_2O); 2.33 (br. *s*, 2 H–C(5')); 2.09 (br. *d*, J = 2.3, 2 H–C(2')); 1.78–1.71 (*m*, 2 H); 1.47 (*t*, J = 6.4, 2 H); 1.39–1.24 (*m*, 2 H); 0.91 (*s*, CH_3–C(1')); 0.14 (*s*, Me_3Si). ^{13}C-NMR (75.5 MHz): 190.18; 161.87; 146.51; 139.23; 138.47; 69.79; 38.67; 36.46; 32.56; 30.71; 24.41; 22.68; 20.81; –1.76. MS: 426 (M^+, (^{35}Cl + ^{37}Cl)), 424 (M^+, (^{35}Cl)), 221 (11), 219 (15), 205 (15), 127 (16, $Me_3SiCHCHCO$), 95 (24), 93 (13), 81 (28), 79 (12), 75 (29), 73 (100, Me_3Si), 71 (21), 69 (13), 57 (35), 55 (47), 53 (14), 45 (11). Anal. calc. for $C_{18}H_{27}Cl_3O_3Si$ (425.85): C 50.77, H 6.39, Cl 24.98; found: C 50.95, H 6.48, Cl 24.99.

(E)-1-(3',4'-Dihydro-2'H-pyranyl)-3-(trimethylsilyl)-2-propen-1-one (**1n**). *Method B.* Yield 82%. B.p. 85°/0.05 Torr. R_f 0.29 (hexane/AcOEt 5:1). IR (neat): 2955*s*, 2900*w*, 2875*w*, 2840*w*, 1735*w*, 1715*w*, 1700*w*, 1680*m*, 1665*m*, 1625*s*, 1585*m*, 1445*w*, 1348*w*, 1306*m*, 1286*s*, 1250*s*, 1217*s*, 1192*m*, 1174*w*, 1091*s*, 1061*s*, 1017*m*, 999*m*, 918*s*, 845*s*, 754*m*, 696*w*, 607*m*. ^{1}H-NMR (300 MHz): 7.28 (*d*, J = 18.7, H–C(2)); 7.05 (*d*, J = 18.7, H–C(3)); 6.08 (*t*, J = 4.2, H–C(5')); 4.13 (*t*, J = 5.0, 2 H–C(2')); 2.25 (*m*, 2 H–C(4')); 1.88 (*m*, 2 H–C(3')); 0.14 (*s*, Me_3Si). MS: 210 (19, M^+), 195 (43), 182 (10), 167 (21), 151 (11), 139 (10), 111 (22), 83 (13), 75 (44), 73 (100), 59 (16), 58 (12), 55 (20), 45 (20), 43 (17). Anal. calc. for $C_{11}H_{18}O_2Si$: C 62.81, H 8.63; found: C 62.62, H 8.84.

(E)-1-[6'-(Benzyloxy)-1'-cyclohexenyl]-3-(trimethylsilyl)-2-propen-1-one (**1p**). *Method B.* Yield 94%. B.p. 130°/0.03 Torr. R_f 0.28 (hexane/AcOEt 8:1). IR: 3090*w*, 3060*w*, 3040*w*, 3005*w*, 2960*s*, 2910*m*, 2885*m*, 1655*s*, 1590*m*, 1500*w*, 1455*m*, 1440*w*, 1420*m*, 1400*m*, 1380*m*, 1350*m*, 1335*m*, 1315*m*, 1250*s*, 1230*s*, 1175*m*, 1160*m*, 1090*s*, 1065*s*, 1030*m*, 990*s*, 960*m*, 925*m*, 860*s*, 840*s*, 770*m*, 750*s*, 740*s*, 700*s*. ^{1}H-NMR (360 MHz): 7.38–7.25 (*m*, Ph); 7.19 (*d*, J = 18.7, H–C(2)); 7.03 (*d*, J = 18.7, H–C(3)); 7.03 (*dd*, J = 4.8, 3.0, H–C(2')); 4.63 (*m*, H–C(6'), 2 H–C(7')); 2.41–1.45 (*m*, 2 H–C(3'), 2 H–C(4'), 2 H–C(5')); 0.18 (*s*, Me_3Si). MS: 223 (0.74, M^+ – $PhCH_2$), 208 (24), 135

(34), 134 (25), 118 (43), 117 (29), 107 (11), 92 (14), 91 (100), 79 (23), 77 (16), 75 (29), 73 (92), 65 (14), 45 (13). Anal. calc. for $C_{19}H_{26}O_2Si$: C 72.56, H 8.35; found: C 7.33, H 8.24.

(E)-1-[2'-(Benzyloxymethyl)-1'-cyclohexenyl]-3-(trimethylsilyl)-2-propen-1-one (**1q**). *Method B.* Yield 83%. R_f 0.24 (hexane/AcOEt 8:1). IR (neat): 3031*w*, 2934*s*, 2859*m*, 1653*s*, 1581*w*, 1497*w*, 1452*m*, 1358*w*, 1307*w*, 1279*m*, 1250*s*, 1225*m*, 1175*w*, 1159*w*, 1111*m*, 1073*m*, 1028*w*, 997*m*, 864*s*, 840*s*, 737*m*, 698*s*. ^{1}H-NMR (300 MHz): 7.33–7.27 (*m*, Ph); 7.07 (*d*, J = 19.1, H–C(2)); 6.58 (*d*, J = 19.0, H–C(3)); 4.39 (*s*, 2 H–C(8')); 3.92 (*s*, 2 H–C(7')); 2.21 (br. *m*, 2 H–C(3'), 2 H–C(6')); 1.68 (*m*, 2 H–C(4'), 2 H–C(5')); 0.13 (*s*, Me_3Si). ^{13}C-NMR (75.5 MHz): 199.0 (C(1)); 148.9 (C(2)); 142.2 (C(3)); 138.2 (C(9')); 136.5 (C(2')); 135.7 (C(1')); 128.3 (C(10')); 127.6 (C(11')); 127.5 (C(12')); 72.5 (C(8')); 71.0 (C(7')); 27.2, 26.8, 22.1 (C(4'), C(5')); −1.8 (Me_3Si). MS: 237 (23), 148 (11), 92 (10), 91 (100), 75 (51), 73 (90), 65 (11), 45 (11), 41 (13). Anal. calc. for $C_{20}H_{28}O_2Si$: C 73.12, H 8.59; found: C 73.31, H 8.41.

(Z)-1-(1'-Cyclopentenyl)-3-(dimethylphenylsilyl)-2-phenyl-2-propen-1-one (**1r**). *Method B.* To CuCN (0.716 g, 8 mmol), (dimethylphenylsilyl)lithium [12] (16 mmol, 22.2 ml of a 0.72M soln. in THF), was added at 0° and the mixture stirred for 20 min. Phenylacetylene (7.2 mmol, 0.735 g) was added in 3 ml THF. TLC indicated the alkyne was consumed within 10 min. 1-Cyclopentene-1-carbonyl chloride (31 mmol; prepared from 1-cyclopentene-1-carboxylic acid with excess oxalyl chloride) was added (exothermic reaction). The mixture was stirred at 0° overnight. An aq. 5% NH_4Cl soln. (5 ml) was added. The product was extracted with Et_2O (3 × 85 ml) from NH_4Cl soln. (45 ml). The org. fractions were washed with NH_4Cl soln. (50 ml) then with brine (50 ml), dried (K_2CO_3), and evaporated. Silica-gel chromatography and bulb-to-bulb distillation gave 0.800 g (34%) of **1r**. B.p. 210°/0.1 Torr. R_f 0.47 (hexane/AcOEt 6:1). IR (CCl_4): 3071*m*, 2959*m*, 1717*w*, 1653*s*, 1611*m*, 1570*w*, 1495*w*, 1445*w*, 1428*m*, 1364*m*, 1296*w*, 1250*s*, 1173*m*, 1115*m*, 1040*w*, 997*w*, 951*w*, 843*s*. ^{1}H-NMR (300 MHz): 7.55–7.25 (*m*, 10 arom. H); 6.47 (br. *s*, H–C(2')); 6.43 (*s*, H–C(3)); 2.48–2.34 (*m*, 4 H); 1.86 (*t*, J = 7.6, 2 H); 0.40 (*s*, Me_2Si). MS: 332 (3.7, $M^{+\cdot}$), 318 (10), 317 (34, $M^{+\cdot}$ − Me), 255 (25, $M^{+\cdot}$ − Ph), 241 (10), 137 (17), 136 (14), 135 (100, $PhMe_2Si$), 105 (13), 95 (29), 67 (11), 43 (12), 41 (12). Anal. calc. for $C_{22}H_{24}OSi$: C 79.47, H 7.28, Si 8.45; found: C 78.99, H 7.30, Si 8.21.

6. Cyclization of Divinyl Ketones to Form Cyclopentenones. – *General Procedure.* Reaction times and temp. are listed in *Tables 5–7*. To the soln. of divinyl ketone **1** in CH_2Cl_2 (0.08M) cooled to the stated temp., 1.05 equiv. of 98% $FeCl_3$ were added. Upon completion (TLC monitoring), an equal volume of H_2O was added and the mixture extracted with Et_2O (3 × 50 ml/g ketone). The org. layers were washed with H_2O (35 ml/g ketone) and brine (3 × 35 ml/g ketone), dried (K_2CO_3), evaporated, immediately chromatographed, and distilled.

Hydrogenation Procedure. To the enone **2** (10–30 mg) in dry AcOEt (5 ml), 5% Pd/C catalyst (0.01 equiv.) was added and the system flushed with H_2 (4×) and then stirred at r.t. under 1 atm of H_2, until the reaction was complete (TLC). The mixture was filtered through *Celite*, the catalyst washed with AcOEt (5 ml), and the filtrate concentrated.

Epimerization Procedure. The saturated ketone (10 mg) was placed in freshly distilled MeOH (1 ml), and 0.05 equiv. of NaOMe (0.2M in MeOH) were added. The mixture was stirred at r.t. and monitored by capillary GC until the ratios became constant.

cis-*3a-Methyl-3a,4,5,6,7,7a-hexahydro-1*H-*inden-1-one* (**2a**). Yield 70%. B.p. 60°/0.3 Torr. R_f 0.30 (hexane/AcOEt 5:1). IR (neat): 3075*w*, 3034*w*, 2932*s*, 2857*m*, 1711*s*, 1582*w*, 1460*m*, 1379*w*, 1350*w*, 1308*w*, 1202*w*, 1169*w*, 1148*w*, 1127*w*, 1067*w*, 893*w*, 862*m*, 845*w*, 793*w*, 758*w*. ^{1}H-NMR (300 MHz): 7.46 (*d*, J = 5.7, H–C(3)); 6.06 (*d*, J = 5.7, H–C(2)); 2.02 (*m*, H–C(7a), H–C(7)); 1.70–1.10 (*m*, 2 H–C(4), 2 H–C(5), 2 H–C(6), H–C(7)); 1.24 (*s*, CH_3). MS: 150 (48, $M^{+\cdot}$), 149 (11), 136 (10), 135 (100), 122 (11), 121 (30), 109 (19), 108 (23), 107 (22), 96 (11), 95 (13), 94 (10), 93 (31), 91 (20), 81 (14), 80 (14), 79 (44), 77 (21), 67 (23), 65 (10), 55 (16), 53 (16), 51 (11), 41 (28), 39 (29). GC: t_R 9.71 min, column *B* (130° isothermal). HR-MS: 150.1039 ($C_{10}H_{14}O$, calc. 150.1045). Anal. calc. for $C_{10}H_{14}O$: C 79.96, H 9.39; found: C 79.61, H 9.03.

*2,2-Dimethyl-2,2aβ,3,4,4aα,5,7aα,7bβ-octahydro-1*H-*cyclobut[e]inden-5-one* (*c,t*-**2b**) *and 2,2-Dimethyl-2,2aβ,3,4,4aβ,5,7aβ,7bβ-Octahydro-1*H-*cyclobut[e]inden-5-one* (*c,c*-**2b**). Yield 70%. B.p. 60°/0.04 Torr. M.p. 62–63°. R_f 0.27 (hexane/AcOEt 5:1). GC: t_R 11.54 min (89%, *c,t*-**2b**) and 12.01 min (11%, *c,c*-**2b**), column *B* (170° isothermal). IR (neat): 2951*m*, 2933*m*, 2864*m*, 1712*s*, 1591*w*, 1465*w*, 1451*w*, 1443*w*, 1383*w*, 1368*w*, 1358*w*, 1339*w*, 1332*w*, 1279*w*, 1261*w*, 1208*w*, 1182*w*, 1174*w*, 1095*w*, 1077*w*, 1059*w*, 982*w*, 962*w*. ^{1}H-NMR (300 MHz): 7.60 (*dd*, J = 5.6, 2.6, 0.85 H, H–C(7)); 7.43 (*dd*, J = 5.7, 2.8, 0.15 H, H–C(7)); 6.22 (*dd*, J = 5.7, 1.9, 0.15 H, H–C(6)); 6.15 (*dd*, J = 5.7, 2.3, 0.85 H, H–C(6)); 3.07 (*tt*, J = 6.9, 2.3, 0.15 H, H–C(7a)); 2.90 (*m*, 0.85 H, H–C(7a)); 2.60 (*dq*, J = 9.1, 2.7, 0.85 H, H–C(7b)); 2.53 (*m*, H–C(4a)); 2.10 (*dddd*, J = 13.8, 12.1, 6.9, 3.1, H–C(4)); 1.92 (*m*, H–C(2a), H–C(1)); 1.74 (*m*, H–C(1), H–C(4)); 1.50–1.20 (*m*, 2 H–C(3)); 1.14 (*s*, CH_3); 0.97 (*s*, CH_3). ^{13}C-NMR (75.5 MHz): 169.4 (C(7)); 133.3 (C(6)); 44.0 (C(7a)); 43.9 (C(4a)); 41.2 (C(2a)); 40.6 (C(1)); 34.8 (C(2)); 30.8 (CH_3); 29.1 (C(7b)); 24.1 (CH_3); 23.3 (C(4)); 20.1 (C(3)). MS: 190 (2, $M^{+\cdot}$), 135 (100), 134 (53), 133 (34), 119 (12), 117 (11), 116 (12), 108 (26), 106 (17), 105 (29), 92 (36), 91 (81), 80 (39), 79 (57), 78 (52), 77 (40), 67 (20), 66 (17), 65 (21), 59

(29), 55 (24), 53 (25), 52 (12), 51 (16), 41 (84), 40 (13), 39 (56). Anal. calc. for $C_{13}H_{18}O$: C 82.06, H 9.53; found: C 82.02, H 9.64.

cis-*3a,4,5,7a-Tetrahydro-5,5-dimethyl-1*H-*inden-1-one* (**2c**). Yield 70%. B.p. 50°/0.05 Torr. R_f 0.23 (hexane/AcOEt 5:1). GC: Column *A* (100° (2 min), 20°/min, 260° (15 min)), t_R 9.15 min. IR (neat): 3022*m*, 2957*s*, 2924*s*, 2864*m*, 1709*s*, 1583*m*, 1470*m*, 1395*w*, 1362*m*, 1345*m*, 1317*w*, 1266*w*, 1213*w*, 1163*s*, 1109*w*, 1082*w*, 988*w*, 959*w*, 909*w*, 804*m*, 776*m*, 750*s*, 723*m*. ^{1}H-NMR (360 MHz): 7.72 (*dd*, *J* = 5.7, 2.8, H–C(3)); 6.11 (*dd*, *J* = 5.8, 1.5, H–C(2)); 5.80 (*dd*, *J* = 9.9, 3.5, H–C(7)); 5.69 (*dd*, *J* = 10.0, 2.5, H–C(6)); 3.27–3.23 (br., H–C(3a)); 2.88 (*m*, H–C(7a)); 1.83 (*dd*, *J* = 12.9, 5.8, H–C(4)); 1.04 (*s*, CH_3); 1.00 (*s*, CH_3); 1.00 (*m*, H–C(4)). MS: 162 (17, M^+), 147 (41), 120 (12), 119 (31), 107 (14), 106 (19), 105 (21), 91 (45), 79 (14), 78 (11), 77 (20), 65 (14) 55 (100), 51 (12), 43 (15), 41 (22), 39 (21), 32 (25), 31 (14). HR-MS: 162.1040 ($C_{11}H_{14}O$, calc. 162.1045). Anal. calc. for $C_{11}H_{14}O$: C 81.44, H 8.69; found: C 81.61, H 8.90.

*7a,7'a-Bi[*cis-*3a,6,7,7a-tetrahydro-6,6-dimethyl-1*H-*inden-1-one]* (**29**). Yield 7%. R_f 0.27 (hexane/AcOEt 5:1). ^{1}H-NMR (200 MHz): 7.64 (*dd*, *J* = 5.9, 2.7, H–C(3)); 6.16 (*dd*, *J* = 6.0, 1.9, H–C(2)); 5.86 (*d*, *J* = 9.8, H–C(6)); 5.72 (*d*, *J* = 9.8, H–C(5)); 3.56 (*m*, H–C(3a)); 1.96 (*dd*, *J* = 13.5, 6.2, H–C(4)); 1.36 (*dd*, *J* = 13.7, 8.9, H–C(4)); 1.14 (*s*, CH_3); 1.00 (*s*, CH_3).

cis-*3a,6,7,7a-Tetrahydro-6,6-dimethyl-1*H-*inden-1-one* (**2d**). Yield 69%. B.p. 85°/2 Torr. M.p. 29–30°. R_f 0.31 (hexane/AcOEt 3:1). GC: Column *B* (130° isothermal), t_R 15.07 min. IR (neat): 3015*m*, 2955*s*, 2867*m*, 1705*s*, 1584*m*, 1468*w*, 1394*w*, 1373*w*, 1361*w*, 1343*w*, 1302*w*, 1261*w*, 1184*m*, 1140*w*, 1076*w*, 1038*w*, 1013*w*, 908*w*, 847*w*, 804*w*, 783*w*, 752*w*, 739*w*, 727*w*, 714*m*, 689*w*. ^{1}H-NMR (300 MHz): 7.56 (*dd*, *J* = 5.7, 2.4, H–C(3)); 6.11 (*dd*, *J* = 5.6, 2.5, H–C(2)); 5.68 (*dd*, *J* = 10.1, 2.1, H–C(5)); 5.61 (*dd*, *J* = 10.1, 3.2, H–C(4)); 3.42 (*m*, H–C(3a)); 2.70 (*dt*, *J* = 9.9, 6.4, H–C(7a)); 1.79 (*dd*, *J* = 13.1, 6.8, H–C(7)); 1.36 (*dd*, *J* = 13.1, 10.0, H–C(7)); 1.02 (*s*, CH_3); 0.93 (*s*, CH_3). MS: 162 (56, M^+), 147 (69), 133 (12), 129 (15), 120 (13), 119 (29), 107 (12), 105 (18), 94 (15), 91 (38), 79 (11), 77 (18), 65 (12), 55 (100), 51 (13), 41 (23), 39 (22). Anal. calc. for $C_{11}H_{14}O$: C 81.45, H 8.70; found: C 81.27, H 8.65.

cis-*5,6,7,7a-Tetrahydrocyclopenta[*b*]pyran-1(3a*H*)-one* (**2e**). Yield 60%. B.p. 50°/0.05 Torr. R_f 0.31 (hexane/AcOEt 2:1). GC: Column *A* (100° isothermal), t_R 14.07 min. IR ($CHCl_3$): 2960 (sh), 2950*m*, 2930 (sh), 2875*m*, 2860*m*, 1720*s*, 1590*w*, 1460*w*, 1455*w*, 1450*m*, 1435*w*, 1380*w*, 1370*w*, 1355*w*, 1345*m*, 1335*m*, 1290*w*, 1280*w*, 1265*m*, 1260*m*, 1250*m*, 1240*m*, 1230*m*, 1195*m*, 1155*m*, 1120*s*, 1105*s*, 1085*m*, 1075*m*, 1055*s*, 1040*m*, 1020*w*, 1000*w*, 970*w*, 960*w*, 920*m*, 900*m*, 870*m*, 865*m*, 860*m*, 810*m*. ^{1}H-NMR (360 MHz): 7.59 (*dd*, *J* = 5.8, 2.6, H–C(7)); 6.34 (*dd*, *J* = 5.8, 1.1, H–C(6)); 4.75 (*dd*, *J* = 5.2, 2.4, H–C(7a)); 3.80 (*dt*, *J* = 11.3, 5.7, H–C(2)); 3.60 (*dt*, *J* = 11.3, 6.8, H–C(2)); 2.37 (*dt*, *J* = 6.9, 5.7, H–C(4a)); 1.87 (*m*, 2 H–C(4)); 1.54 (*m*, 2 H–C(3)). MS: 138 (27, M^+), 137 (13), 121 (12), 110 (36), 109 (18), 108 (12), 96 (11), 95 (22), 84 (55), 83 (21), 82 (95), 81 (25), 80 (12), 79 (37), 77 (16), 69 (19), 68 (29), 67 (16), 66 (11), 65 (10), 55 (100), 54 (23), 53 (29), 52 (25), 51 (21), 50 (11), 41 (31), 40 (12), 39 (57). Anal. calc. for $C_8H_{10}O_2$: C 69.54, H 7.30; found: C 69.22, H 7.30.

Methyl cis-*3a,4,5,6,7,7a-Hexahydro-1-oxo-1*H-*cyclopenta[*b*]pyridine-4-carboxylate* (**2h**). Cyclization was accomplished using 3 equiv. of $ZrCl_4$ in CH_2Cl_2, 60° for 36 h. Yield 76%. B.p. 160°/0.5 Torr. R_f 0.31 (Et_2O). IR (CCl_4): 3854*w*, 3422*w*, 2955*s*, 2867*m*, 2359*m*, 1709*vs*, 1592*w*, 1539*w*, 1447*vs*, 1402*s*, 1367*s*, 1343*s*, 1318*s*, 1256*s*, 1192*s*, 1167*m*, 1123*m*, 1102*m*, 1084*m*, 1044*m*, 1007*w*, 938*w*, 889*w*. ^{1}H-NMR (200 MHz): 7.59–7.51 (br. *s*, H–C(3)); 6.30 (*dd*, *J* = 3.8, 1.9, H–C(2)); 5.43–5.26 (br. *d*, H–C(3a)); 4.0–3.8 (br. *s*, H–C(7a)); 3.75 (*s*, CH_3O); 3.5–2.88 (*m*, H–C(5)); 3.72–3.65 (*m*, H–C(5)); 1.90–1.76 (*m*, 2 H); 1.6–1.37 (*m*, 2 H). MS: 195 (4, M^+), 168 (13), 167 (100, $M^+ - CO$), 166 (33), 152 (26), 141 (25), 140 (15), 138 (12), 136 (52, $M^+ - CH_3OCO$), 135 (12), 108 (41), 107 (12), 106 (10), 94 (13), 91 (10), 82 (15), 81 (15), 80 (26), 79 (26), 77 (21), 68 (12), 67 (13), 66 (13), 65 (14), 59 (34), 55 (26), 54 (22), 53 (33), 52 (23), 51 (14), 42 (36), 41 (38), 40 (10), 31 (17).

cis-*3a,4,5,6,7,7a-Hexahydro-3-methyl-1*H-*inden-1-one* (**2i**). Yield 76%. B.p. 100°/0.07 Torr. R_f 0.21 (hexane/AcOEt 4:1). IR (neat): 3065*w*, 2932*s*, 2855*s*, 2361*w*, 2336*w*, 1701*vs*, 1617*s*, 1559*w*, 1539*w*, 1507*w*, 1437*s*, 1377*m*, 1314*m*, 1298*m*, 1235*w*, 1181*m*, 1169*m*, 1127*m*, 1076*w*, 1024*w*. ^{1}H-NMR (500 MHz): 5.79 (*s*, H–C(2)); 2.69 (*dd*, *J* = 15.2, 6.6, H–C(3a)); 2.37 (*dd*, *J* = 12.2, 6.3, H–C(7a)); 2.01 (*s*, CH_3); 1.96–1.90 (*m*, 1 H); 1.86–1.79 (*m*, 1 H); 1.60–1.53 (*m*, 1 H); 1.48–1.40 (*m*, 2 H); 1.30–1.23 (*m*, 1 H); 1.19–1.13 (*m*, 1 H); 1.07–1.00 (*m*, 1 H). ^{13}C-NMR (125 MHz): 211.03; 181.14; 128.29; 46.52; 43.82; 27.40; 22.31; 21.31; 21.11; 17.28. MS: 151 (14, $M^+ + H$), 150 (99, M^+), 149 (16), 135 (52, $M^+ - CH_3$), 122 (24), 121 (100), 109 (48), 108 (14), 107 (13), 96 (39), 93 (12), 79 (14). Anal. calc. for $C_{10}H_{14}O$ (150.22): C 79.93, H 9.47; found: C 79.95, H 9.39.

cis-*3a,4,5,6,7,7a-Hexahydro-2-(2'-propenyl)-1*H-*inden-1-one* (**2j**). Yield 76%. B.p. 90°/0.1 Torr. R_f 0.47 (hexane/AcOEt 4:1). IR (CCl_4): 3750*w*, 3407*w*, 3085*w*, 2936*m*, 2859*m*, 2363*w*, 1709*vs*, 1642*w*, 1449*w*, 1360*w*, 1252*w*, 1196*w*, 995*w*, 918*m*, 808*w*. ^{1}H-NMR (200 MHz): 7.26 (*dd*, *J* = 2.9, 1.3, H–C(3)); 5.91–5.81 (*m*, CH=CH_2); 5.15–5.05 (*m*, CH=CH_2); 2.97–2.86 (*m*, CH_2–CH=CH_2, H–C(3a)); 2.46 (*q*, H–C(7a)); 1.92–1.30 (*m*, 8 H). MS:

176 (98, $M^{+\cdot}$), 175 (14), 161 (47), 148 (59), 135 (39), 134 (27), 133 (42), 121 (13), 120 (13), 119 (28), 117 (16), 109 (69), 108 (12), 107 (26), 106 (18), 105 (59), 103 (11), 95 (52), 94 (12), 93 (21), 92 (27), 91 (100), 81 (55), 80 (29), 79 (99), 78 (32), 77 (72), 67 (88), 66 (30), 65 (44), 63 (14), 55 (21), 54 (18), 53 (45), 52 (17), 51 (29), 41 (99), 40 (16), 39 (96). Anal. calc. for $C_{12}H_{16}O$: C 81.77, H 9.15; found: C 81.67, H 8.94.

*cis-3a,4,5,6,7,7a-Hexahydro-5,5-dimethyl-1*H*-inden-1-one* (**2k**). Yield 78%. B.p. 50°/0.05 Torr. R_f 0.38 (hexane/AcOEt 4:1). IR (neat): 3080*w*, 3045*w*, 2940*s*, 2860*s*, 1705*s*, 1650 (sh), 1580*m*, 1460*s*, 1385*m*, 1365*m*, 1345 (sh), 1335*m*, 1315*m*, 1270*w*, 1250*w*, 1210*m*, 1190 (sh), 1170*s*, 1140*m*, 1115*m*, 1090*m*, 1050*m*, 990*w*, 950*m*, 915*w*, 900*m*, 890*w*, 870*w*, 830*m*, 810*w*, 770*m*, 740*m*, 720*m*. ^{1}H-NMR (360 MHz): 7.69 (*dd*, *J* = 5.7, 3.0, H–C(3)); 6.11 (*dd*, *J* = 5.6, 1.1, H–C(2)); 3.02 (*m*, H–C(3a)); 2.38 (*dd*, *J* = 13.5, 6.1, H–C(7a)); 1.90–1.66 (*m*, 4 H); 1.27–1.08 (*m*, 2 H), 0.96 (*s*, CH_3); 0.89 (*s*, CH_3). MS: 165 (12), 164 (92, $M^{+\cdot}$), 149 (52), 135 (12), 131 (16), 122 (12), 121 (30), 109 (40), 108 (48), 107 (53), 105 (14), 96 (26), 95 (100), 94 (24), 93 (31), 91 (21), 82 (14), 81 (27), 80 (30), 79 (61), 78 (10), 77 (34), 69 (24), 68 (13), 67 (36), 66 (22), 65 (16), 55 (36), 53 (28), 52 (11), 43 (12), 41 (66), 40 (12), 39 (42). Anal. calc. for $C_{11}H_{16}O$: C 80.45, H 9.81; found: C 80.10, H 9.92.

Hydrogenation: Yield 95%. GC: t_R 8.86 min (*cis*-**2k**·H_2), column *A* (150° (2 min), 5°/min, 250° (10 min)).

Epimerization: GC (as above): t_R 8.69 min (14%, *trans*-**2k**·H_2) and 8.86 min (86%, *cis*-**2k**·H_2).

*3-(*cis*-3a,4,5,6,7,7a-Hexahydro-5-methyl-1-oxo-1*H*-inden-5-yl)propyl Trichloroacetate* (**2m**). Yield 78%. R_f 0.32 (hexane/AcOEt 2:1). IR (CCl_4): 2922*m*, 1753*s*, 1711*m*, 1232*s*, 978*w*, 823*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.68 (*dd*, *J* = 5.7, 2.6, H–C(2)); 3.1–2.9 (*m*, H–C(3a)); 2.42–2.34 (*m*, H–C(7a)); 1.83–1.05 (*m*, 10 H); 0.95 (*s*, 1.5 H, CH_3); 0.84 (*s*, 1.5 H, CH_3). MS: 356 (2, $M^{+\cdot}$ + 4), 354 (7, $M^{+\cdot}$ + 2), 352 (7, $M^{+\cdot}$), 150 (11), 149 (100), 147 (15), 131 (12), 121 (19), 108 (21), 107 (22), 105 (14), 96 (12), 95 (44), 94 (13), 93 (13), 86 (42), 84 (74), 82 (24).

cis-*3a,4,5,6,7,7a-Hexahydro-5-(3-hydroxypropyl)-5-methyl-1*H*-inden-1-one* (**2s**). A mixture of (*c,c*)- and (*c,t*)-**2m** was subjected to repeated silica-gel chromatography to obtain a sample of 1 of the diastereoisomers (bearing a Me group with δ 0.94 ppm) in pure form. A soln. of 40.0 mg of that isomer in abs. EtOH (5 ml) was stirred with *ca.* 0.5 g of $NaHCO_3$ at r.t. Hydrolysis was complete in 1 h; the mixture was immediately filtered and the soln. evaporated under reduced pressure. Chromatography afforded 21.0 mg (89%) of pure **2s**. GC: no ring-fusion isomers or other contaminants. IR (CCl_4): 3638*w*, 3465*m*, 2938*s*, 2889*m*, 1767*s*, 1601*w*, 1499*m*, 1418*m*, 1362*m*, 1200*w*, 1103*m*, 963*w*, 939*m*, 847*w*, 822*w*. ^{1}H-NMR (300 MHz): 7.69 (*dd*, *J* = 5.6, 2.9, H–C(3)); 6.12 (*dd*, *J* = 5.6, 0.9, H–C(2)); 3.59 (*t*, *J* = 6.5, CH_2O); 3.03–3.00 (br. *s*, H–C(3a)); 2.39 (*q*, *J* = 6.7, H–C(7a)); 1.82–1.45 (*m*, 6 H); 1.22–1.17 (*m*, 4 H); 0.94 (*s*, CH_3); 0.83 (*t*, *J* = 12.5, 1 H). MS: 208 (22, $M^{+\cdot}$), 150 (13), 149 (100, $M^{+\cdot} - C_3H_6OH$), 148 (10), 131 (19), 121 (15), 109 (13), 108 (28), 107 (14), 105 (14), 96 (12), 95 (33), 94 (10), 93 (15), 84 (14), 81 (11). HR-MS: 208.1456 ($C_{13}H_{20}O_2$, calc. 208.1463).

Deprotection of a mixture of diastereoisomeric trichloroacetates **2m** afforded a mixture **2s**/**2s′**. B.p. 180°/0.4 Torr. ^{1}H-NMR (300 MHz): 7.68 (*dd*, *J* = 5.6, 2.9, H–C(3)); 6.12 (*d*, *J* = 5.6, H–C(2)); 3.65 (*t*, *J* = 6.4, CH_2O); 3.03–2.98 (*m*, H–C(3a)); 2.38 (*q*, *J* = 6.6, H–C(7a)); 1.82–1.07 (*m*, 10 H); 0.84 (*s*, CH_3); 0.79 (*t*, *J* = 12.6, 1 H).

cis-*4,5,6,6a-Tetrahydro-2-phenylpentalen-1(3a*H*)-one* (**2r**). Yield 86%. B.p. 110°/0.15 Torr. R_f 0.38 (hexane/AcOEt 4:1). IR (CCl_4): 3401*w*, 3061*w*, 3036*w*, 2955*s*, 2870*m*, 2336*w*, 1948*w*, 1804*w*, 1707*vs*, 1553*s*, 1495*m*, 1449*s*, 1325*m*, 1304*m*, 1256*m*, 1177*w*, 1334*w*, 1111*m*, 1075*m*, 1005*m*, 980*m*, 936*m*, 887*m*. ^{1}H-NMR (300 MHz): 7.79–7.10 (*m*, Ph, H–C(3)); 3.36–3.22 (*m*, H–C(6a)); 2.93–2.83 (*m*, H–C(3a)); 2.04–1.17 (*m*, 6 H). MS: 199 (15, $M^{+\cdot}$ + 1), 198 (100, $M^{+\cdot}$), 170 (41), 169 (21), 155 (19), 142 (59), 141 (53), 131 (19), 129 (14), 128 (21), 115 (26), 103 (35), 102 (36), 91 (15), 77 (14, Ph), 76 (11), 67 (16), 51 (13), 41 (14), 39 (18). Anal. calc. for $C_{14}H_{14}O$: C 84.81, H 7.12; found: C 84.93, H 7.22.

*3a,4,5,6,7,7a-Hexahydro-1-methyl-1*H*-inden-1-ol* (**27**). A round-bottomed flask containing 7.45 g of $CeCl_3 \cdot 7 H_2O$ (0.020 mmol) was heated under high vacuum to 140° for 1 h. A stirring bar was added and the flask again heated to 140° under vacuum, this time with stirring, for 1 h. The flask was then cooled to 0°, and 160 ml of THF were added. The suspension was stirred for 2 h at r.t., then cooled to −78°. MeLi (17.4 ml of a 1.15M soln. in Et_2O; 0.020 mol) was added and the mixture stirred for 1 h at −78°. A soln. of *cis*-3a,4,5,6,7,7a-hexahydro-1*H*-inden-1-one in THF (10 ml) was added *via* syringe. After 10 min, the mixture was quenched with 4% aq. NH_4Cl soln. (100 ml). The product was extracted with Et_2O (3 × 200 ml), and the org. extracts were washed with H_2O (2 × 80 ml) and brine (1 × 80 ml), dried (K_2CO_3), and concentrated. Bulb-to-bulb distillation (120°/0.4 Torr) provided 1.38 g (91%) of pure **27**. IR (neat): 3443*s*, 3046*s*, 2896*s*, 2664*m*, 1703*s*, 1617*m*, 1449*s*, 1370*s*, 1229*s*, 1190*s*, 1111*s*, 1059*s*, 1034*s*, 968*s*, 930*s*, 909*s*, 889*m*, 857*m*, 843*m*, 833*m*. ^{1}H-NMR (300 MHz): 5.77 (*dt*, *J* = 5.6, 1.8, H–C(3)); 5.65 (*d*, *J* = 5.6, H–C(2)); 2.62 (*m*, H–C(3a)); 1.3 (*s*, CH_3). ^{13}C-NMR (75.5 MHz): 137.38 (C(2), C(3)); 84.15; 46.89; 43.27; 29.95; 25.56; 23.86; 23.58; 22.54. MS: 152 (60, $M^{+\cdot}$), 138 (10), 137 (100, $M^{+\cdot}$ − Me), 119 (10), 109 (39), 95 (20), 94 (99), 93 (12), 91 (12), 84 (14), 82 (13), 81 (12), 79 (26), 71 (26), 67 (31). Anal. calc. for $C_{10}H_{16}O$: C 78.90, H 10.59; found: C 78.66, H 10.56.

To a soln. of pyridine (0.53 ml, 6.57 mmol) in CH_2Cl_2 was added 329 mg of CrO_3 (3.29 mmol). After stirring at r.t. for 15 min, the mixture was cooled to 0° and a soln. of **27** (167 mg, 1.10 mmol) was added in CH_2Cl_2 (7 ml). The soln. was permitted to warm to r.t. After 2 h, an additional equiv. of $CrO_3 \cdot 2py$ was added in CH_2Cl_2 (15 ml). The reaction was completed within 30 min; the soln. was filtered through *Celite*, and the salts were washed with acetone (2 × 50 ml). The soln. was evaporated and filtered through a plug of silica gel with Et_2O. Chromatography (hexane/AcOEt 4:1) and bulb-to-bulb distillation (100°/0.07 Torr) provided an 81% yield of pure **2i** with spectroscopic properties identical to those listed above.

REFERENCES

[1] a) S. E. Denmark, T. K. Jones, *J. Am. Chem. Soc.* **1982,** *104,* 2642; b) T. K. Jones, S. E. Denmark, *Helv. Chim. Acta* **1983,** *66,* 2377; c) T. K. Jones, S. E. Denmark, *ibid.* **1983,** *66,* 2397; d) S. E. Denmark, K. L. Habermas, G. A. Hite, T. K. Jones, *Tetrahedron* **1986,** *42,* 2821.

[2] a) S. E. Denmark, T. K. Jones, *Org. Synth.* **1985,** *64,* 182; b) S. E. Denmark, T. K. Jones, *J. Org. Chem.* **1985,** *50,* 4037; c) S. E. Denmark, T. K. Jones, *ibid.* **1982,** *47,* 4595.

[3] V. F. Mironov, A. D. Petrov, N. D. Maksimova, *Bull. Acad. Sci. USSR, Ser. Chem. Sci. (Engl. Transl.)* **1959,** 1864.

[4] J.-L. Luche, A. L. Gemal. *J. Am. Chem. Soc.* **1981,** *103,* 5454.

[5] H. Firouzabadi, Z. Moostafavipoor, *Bull. Chem. Soc. Jpn.* **1983,** *56,* 914.

[6] G. Stork, M. E. Jung, E. Colvin, Y. Noel, *J. Am. Chem. Soc.* **1974,** *96,* 3685.

[7] E. J. Corey, J. W. Suggs, *Tetrahedron Lett.* **1975,** 2647.

[8] J. G. Duboudin, B. Jousseaume, *J. Organomet. Chem.* **1979,** *168,* 1.

[9] A. R. Chamberlin, J. E. Stemke, F. T. Bond, *J. Org. Chem.* **1978,** *43,* 147.

[10] G. Stork, R. L. Danheiser, *J. Org. Chem.* **1973,** *38,* 1775.

[11] R. K. Boeckman, K. J. Bruza, *Tetrahedron* **1981,** *37,* 3997.

[12] I. Fleming, T. W. Newton, F. Roessler, *J. Chem. Soc., Perkin Trans. 1* **1981,** 2527.

[13] H. O. House, G. H. Rasmussen, *J. Org. Chem.* **1963,** *28,* 31.

[14] a) J. R. Anderon, C. E. Briant, R. L. Edwards, R. P. Mabelis, J. P. Payser, H. Spencer, A. J. S. Whalley, *J. Chem. Soc., Chem. Commun.* **1984,** 405; b) L. A. Paquette, T. Sugimura, *J. Am. Chem. Soc.* **1986,** *108,* 3841.

[15] C. D. Gutsche, D. Redmore, in 'Carbocyclic Ring Expansion Reactions', Academic Press, New York, 1968.

[16] P. E. Petersen, R. L. B. Lefew, B. L. Jensen, *J. Org. Chem.* **1986,** *51,* 1948.

[17] G. Cainelli, C. Cardillo, 'Chromium Oxidation in Organic Chemistry', Springer Verlag, Berlin, 1984, Chapt. 4.

[18] T. Imamoto, T. Kusumoto, Y. Tawarayama, Y. Sugiura, T. Mita, Y. Hatanaka, M. Yokoyama, *J. Org. Chem.* **1984,** *49,* 3904.

[19] R. Radcliffe, R. Rodehorst, *J. Org. Chem.* **1970,** *35,* 4000.

[20] P. Sundararaman, W. Herz, *J. Org. Chem.* **1977,** *42,* 813.

[21] M. A. Tius, D. P. Astrab, A. H. Fang, J.-B. Ousset, S. Trehan, *J. Am. Chem. Soc.* **1986,** *108,* 3438.

[22] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978,** *43,* 2923.

[23] a) K. E. Harding, R. C. Ligon, *Synth. Commun.* **1974,** *4,* 297; b) G. Piancatelli, G. D'ottari, A. Scretti, *Ann. Chim.* **1972,** *62,* 394; c) T. Shono, Y. Matsumura, K. Tsubata, A. Sugihara, S.-I. Yamane, T. Kanazowa, T. Aoki, *J. Am. Chem. Soc.* **1982,** *104,* 6697; d) Y. Chan, W. W. Epstein, *Org. Synth.* **1973,** *53,* 48; e) I. R. Robertson, J. T. Sharp, *Tetrahedron* **1984,** *40,* 3095; f) K. Takeda, Y. Shimono. E. Yoshii, *J. Am. Chem. Soc.* **1983,** *105,* 563; g) A. B. Smith, S. J. Branca, N. P. Pilla, M. A. Guaciaro, *J. Org. Chem.* **1982,** *47,* 1855; h) R. M. Coates, P. D. Senter, W. R. Baker, *ibid.* **1982,** *42,* 3597; i) K.-H. Schulte-Elte, B. Willhalm, F. Gautschi, to *Firmenich SA,* U.S. Patent 4,147,672, 1979; j) J. J. Panouse, C. Sannié, *Bull. Soc. Chim. Fr.* **1956,** 1272.

[24] P. Vitorelli, J. Peter-Katalinic, A. Mukherjee-Mueller, H.-J. Hansen, H. Schmid, *Helv. Chim. Acta* **1975,** *58,* 1379.

[25] D. Seebach, H. Newmann, *Chem. Ber.* **1974,** *107,* 847.