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SILICON-DIRECTED NAZAROV CYCLIZATIONS—IV

FURTHER STUDIES IN STEREOCHEMICAL CONTROL

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Abstract—The silicon-directed Nazarov cyclization was shown to proceed with good to excellent stereoselectivity in cyclohexenyl systems bearing a variety of ring substituents. In all cases the *trans* family of isomers predominated, and *cis* ring-fused products were formed exclusively. The potential for stereocontrol by increasing the bulk of silicon substituents was limited for five-membered rings and good for six-membered rings. Phenylsilanes were found to participate in cyclization.

INTRODUCTION

The challenges to modern synthetic methodology posed by biologically active cyclopentanoid natural products and structurally intriguing polyquinanes[1] have stimulated much activity. The myriad of structural settings in which cyclopentanes can be found in nature [acyclic (prostanoids[2]), polycyclic (iridoids,[3] pseudoguaianes,[4] ophiobolins,[5] triquinanes[1])] presents a particular challenge to general methodology. The successful realization of many of these synthesis targets bears witness to the utility of the new methods. An additional reward is the bounty of new reactions which have been conceived, developed or modified to provide solutions to cyclopentane construction. Among the more notable developments are: trimethylenemethane cycloadditions (Pd complexes,[6] diyls[7]), oxyallyl cation cycloadditions,[8] vinylcyclopropane rearrangements,[9] ene-reactions,[10] domino Diels–Alder reactions,[11] *meta* photocycloadditions,[12] silylcyclopentene annulation[13] and α-alkynone cyclization.[14]

Our interest in this area has focused on the following aspects of penta-annelation:[15] (1) generality of application to various substrates; (2) reagent-based approach to precursors; (3) regio- and stereocontrol; and (4) potential for synthetic manipulation of substrates. We[16] have recently described our efforts in meeting these criteria by modification of the classical Nazarov cyclization of divinylketones, 1 (Scheme 1). While the Nazarov reaction has found extensive use in synthesis[17] it is nevertheless hampered by drawbacks: (1) lack of control over the position of unsaturation; (2) lack of stereocontrol in annelations; and (3) competing cationic side reactions.[18] By making use of the well-documented β-cation-stabilizing effect of silicon[19] we have been able to preordain the collapse of related cation **iii** to dienolate **iv** which leads to cyclopentenones of the type **4** (Scheme 2). In its role here, the trimethylsilyl group serves several useful functions: (1) it guarantees placement of the double bond in the thermodynamically less favorable position; (2) it suppresses undesirable side reactions; and (3) it allows the pericyclic nature of the process to be expressed.[20] Thus, we can take advantage of coupled nuclear motions to control and predict the creation of ring fusion stereocenters (Scheme 3). In a preliminary study[16c] we examined the remote stereocontrol of simple alkyl substituents in **5**. The present study was undertaken to: (1) expand the range of substituents, R, for stereocontrol; and (2) to evaluate in detail the effects of silicon substituents, R′, in five- and six-membered rings.

RESULTS

A. *Substituents on ring*

To evaluate the remote stereocontrolling effect of various substituents we selected groups of varying bulk as well as those which embodied synthetic potential. In this study we have examined vinyl (**5b**), phenyl (**5c**), t-butyl (**5d**), benzyloxymethyl (**5e**) and benzyloxy (**5f**) groups. Divinyl ketones **5b–e** were prepared in the usual manner[16b] from the corresponding aldehydes which were, in turn, obtained by a method developed in these laboratories[21] (Scheme 4). Substrate **5f**

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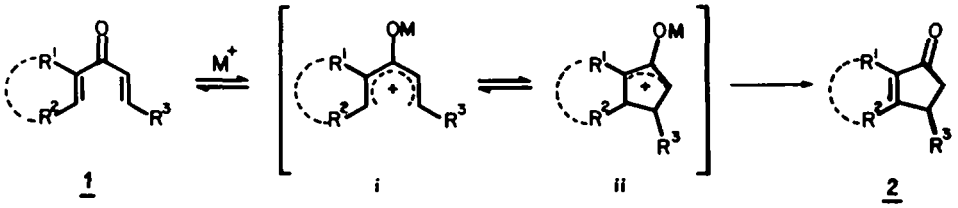
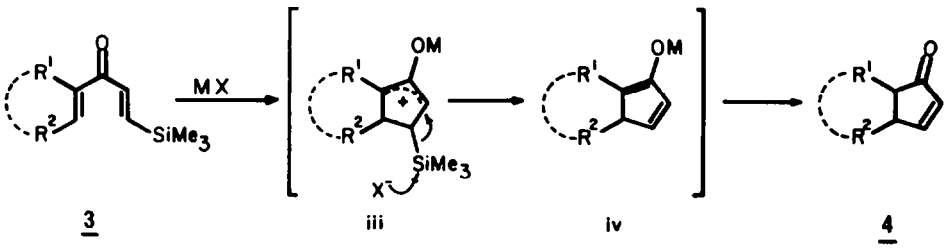
‡ Taken in part from the Ph.D. Thesis of T.K.J., University of Illinois, Urbana, 1984.

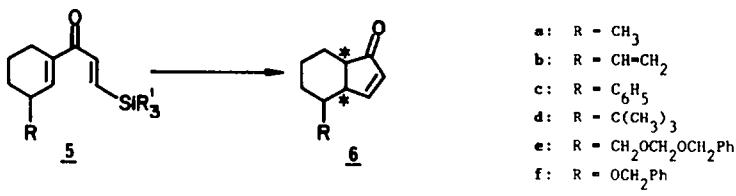
§ ACS Organic Division Fellow 1983–1984.



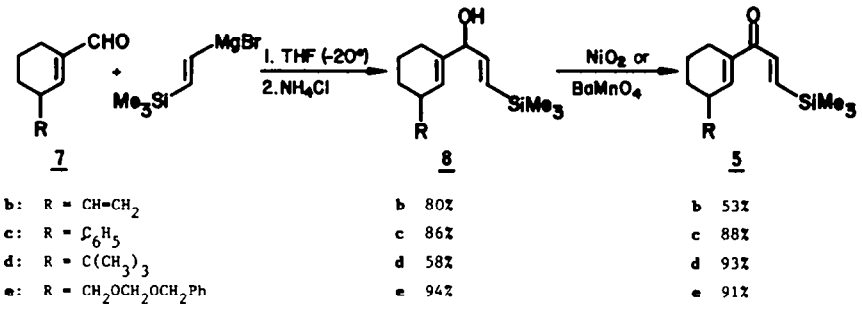
Scheme 1.



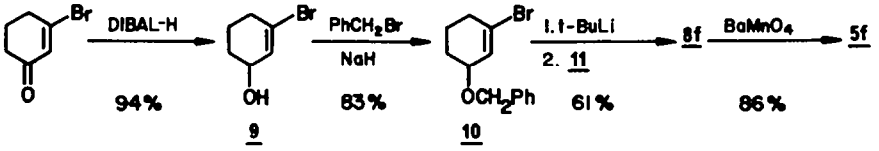
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

was prepared in a straightforward fashion from 3-bromocyclohexenone and *E*-3-trimethylsilyl-2-propenal (**11**) as shown in Scheme 5.

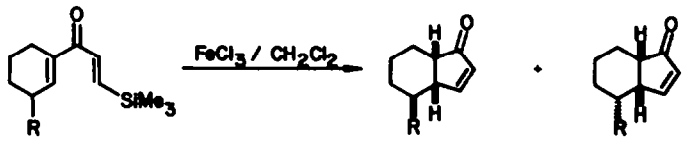
The Nazarov cyclizations were all conducted with $FeCl_3$ in dichloromethane at 0° or below. The results of those cyclizations are collected in Table 1. The reactions all proceed in good yield with the exception of **5e**, which suffers considerable deprotection under the reaction conditions. It is interesting to note that the benzyloxy group of **5f** survives. In all cases stereoisomeric mixtures of *cis*-fused compounds **6** were produced.† Simple alkyl substituents (**5a,b**) had only moderate effects (selectivity *ca* 3:1) while sterically demanding groups gave selectivities in excess of 10:1. The ratios of stereoisomers were established by either capillary GC or ^{1}H-NMR analysis of purified but unresolved reaction mixtures.

In our previous work we found that an unambiguous assignment of stereochemistry was not possible using spectroscopy alone and we resorted to conformation analysis. Thus for **6b** hydrogenation (which locks the stereochemical families) produced a 69:4:27 mixture of isomers which upon equilibration with $NaOCH_3$–CH_3OH gave a 39:31:4:26 mixture. The picture most consistent with these results is shown in Scheme 6. Since stereochemical families (i.e. pairs of C-4 epimers) cannot interconvert, pairwise sums lead to the ratio of families in the original cyclization mixture (70:30). Furthermore, the ratio of *cis* and *trans* ring fusion isomers within each family allows clear assignment. In the *trans* family the ethyl group can be equatorial in both while in the *cis* family the ethyl group must be axial in the (*T,C*)-isomer. Thus, the assignment follows and the ratio of (*C*, *T*)-H_4-**6b** to (*T,T*)-H_4-**6b** is 1.3:1, the same as we observed for **6a**.[16c]

This procedure was not necessary for the other cyclization products since we have now collected enough examples to allow reasonable assignment by ^{1}H-NMR spectroscopy. Table 2 contains all the pertinent data which are used to assign structures.

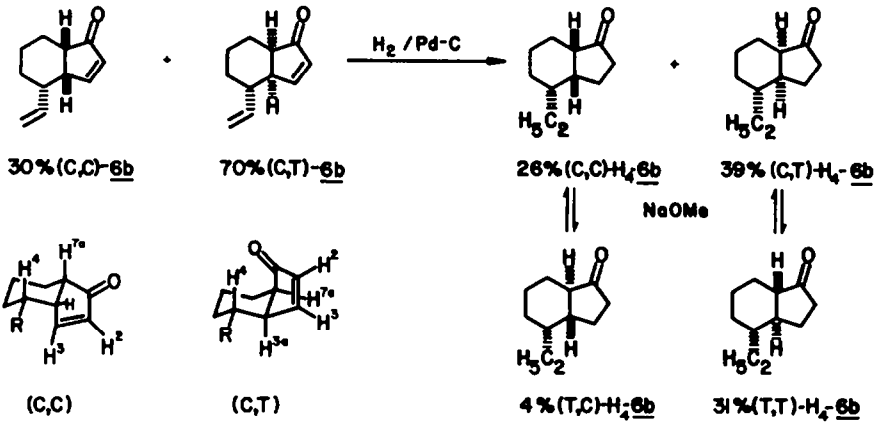
† The stereochemical descriptors specify ring fusion and stereochemical family, respectively. The family is defined by the relationship between H-C(3a) and H-C(4).[16c]

Table 1. Nazarov cyclization of **5a–f**



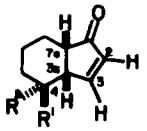
Substrate	R	Time (h)	Temp (°)	(*C,T*)	(*C,C*)	Yield (%)
5a	CH_3	4	0	78	22	99[a]
5b	$CH{=}CH_2$	2	−10	70	30	66
5c	C_6H_5	4	0	94	6	76
5d	$C(CH_3)_3$	8	0	94	6	63
5e	$CH_2OCH_2OCH_2Ph$	2	0	93	7	40[b]
5f	OCH_2Ph	2	0	90	10	76[c]

[a] Ref. 16*c*.
[b] Low yield due to deprotection.
[c] 90/10 is minimum selectivity, 3% of a *trans*-fused isomer was also detected.



Scheme 6.

Table 2. ^{1}H-NMR chemical shifts and coupling constants for **6b–f**



Compound	Substituents	H-C(2)	H-C(3)	H-C(3a)	H-C(4)	H-C(7a)
(*C,T*)-**6b**	$R^1 = CH{=}CH_2$; $R^2 = H$	6.15	7.74	2.70	2.03	2.42
(*C,C*)-**6b**	$R^1 = H$; $R^2 = CH{=}CH_2$	6.23	7.53	3.18	2.03	2.52
(*C,T*)-**6c**	$R^1 = C_6H_5$; $R^2 = H$	6.17	7.50	3.06	—	2.55
(*C,T*)-**6d**	$R^1 = C(CH_3)_3$; $R^2 = H$	6.16	7.57	3.12	2.14	2.25
(*C,T*)-**6e**	$R^1 = CH_2OCH_2OBn$; $R^2 = H$	6.15	7.87	2.78	—	2.41
(*C,C*)-**6e**	$R^1 = H$; $R^2 = CH_2OCH_2OBn$	6.25	7.66	3.32	—	2.50
(*C,T*)-**5f**	$R^1 = OCH_2Ph$; $R^2 = H$	6.18	7.84	3.02	3.14	2.48

Compound	Substituents	J(2,3a)	J(3,3a)	J(4,3a)	J(3a,7a)
(*C,T*)-**6b**	$R^1 = CH{=}CH_2$; $R^2 = H$	1.2	3.0	·	6.2
(*C,C*)-**6b**	$R^1 = H$; $R^2 = CH{=}CH_2$	2.2	2.3	—	6.2
(*C,T*)-**6c**	$R^1 = C_6H_5$; $R^2 = H$	1.6	3.1	10.0	6.3
(*C,T*)-**6d**	$R^1 = C(CH_3)_3$; $R^2 = H$	1.6	3.2	—	6.3
(*C,T*)-**6e**	$R^1 = CH_2OCH_2OBn$; $R^2 = H$	1.4	3.0	9.8	6
(*C,C*)-**6e**	$R^1 = H$; $R^2 = CH_2OCH_2OBn$	2.2	2.5	5	5
(*C,T*)-**6f**	$R^1 = OCH_2Ph$; $R^2 = H$	1.3	2.4	8.5 or 9.5	—

Many of the coupling constants were determined by double-resonance techniques. First, the magnitude of the H-C(3a)/H-C(7a) coupling constant which could be located in nearly every case is indicative of a *cis* ring fusion (5–6 Hz). Second, in those cases where the H-C(3a)/H-C(4) coupling constant could be determined (**5c, e, f**), the major isomer shows large coupling (9–10 Hz) indicative of a (*C,T*)-isomer with the diaxial relationship of these hydrogens.

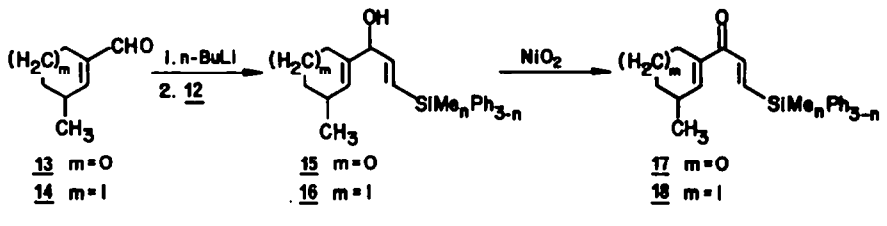
Finally, a trend noted in our earlier work is further documented here in the magnitude of the J_{2-3a} and J_{3-3a} couplings for (*C,T*)- and (*C,C*)-isomers. When the cyclopentenone ring has an axial carbonyl group [(*C,T*) in this series] $J_{3,3a} > J_{2,3a}$ due to the dihedral angle dependence of allylic couplings.[22] However, in the isomer which has an equatorial carbonyl group [(*C,C*) in this series], $J_{3,3a} \sim J_{2,3a}$ since the allylic coupling should be a maximum here. In summary, we have found that very good relative stereocontrol can be obtained with various substituents in the silicon-directed Nazarov cyclization and that the stereochemical course can be interpreted in terms of steric approach control to the less-hindered face of the cyclohexenyl unit.

B. *Silicon substituents*

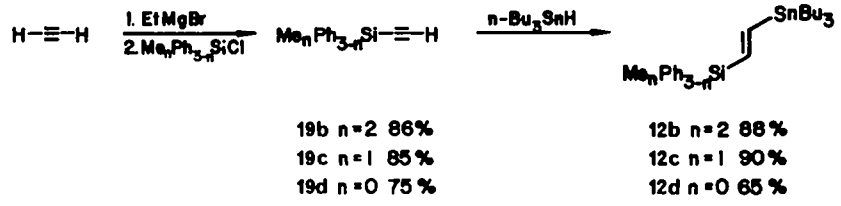
The results from the previous section clearly demonstrate a steric component on the selection between the two allowed conrotatory pathways leading to (*C,T*)- and (*C,C*)-isomers. If the preference for production of the (*C,T*)-isomer is indeed steric approach control to the less-hindered face of the endocyclic olefin, then the bulk of the "attacking" vinylsilane unit should also be significant. In this capacity the silyl moiety would serve a second role as a phantom directing group. There is good reason to expect non-bonding interactions of the terminal ligands to play a role by analogy to the well-documented effects in the opening of cyclopropyl cations.[23] In our previous study we demonstrate the feasibility of this kind of control by incorporating a triisopropylsilyl group with reasonable success.[16c] The study described here is a systematic examination of the stereochemical response to substitution by dimethylphenyl-, diphenylmethyl- and triphenylsilyl groups to the cyclization in five- and six-membered ring systems. In all cases the remote stereocenter bears only a methyl group; thus, the degree of stereocontrol will represent the lower limit for substituents at that position.

(B.1) *Preparation of substrates.* The methods used to prepare the precursors for cyclization were those employed previously in the synthesis of the triisopropyl derivative. The general approach outlined in Scheme 7 required the various vinylstannanes **12b–d**. The trimethylsilyl series (**a** : $n = 3$) was prepared in the usual way from *E*-(2-bromoethenyl)trimethylsilane as shown in Scheme 4. The tin reagents were prepared by the hydrostannylation of the corresponding silylacetylenes using an equimolar amount of tributyltin hydride.[24] The silylacetylenes were in turn prepared by silylation of ethynylmagnesium bromide. The overall yields from commercially available chlorosilanes were very good (Scheme 8). Transmetallation with n-BuLi and addition of the vinyllithiums to aldehydes **13** and **14** proceeded cleanly to afford the divinyl carbinols **15** and **16**, which were oxidized without exception using NiO_2.

(B.2) *Nazarov cyclizations.* Each of the ring sizes will be discussed separately since the results and the methods of stereochemical assignment vary widely. In all cases the reactions were done in CH_2Cl_2 using 1.05 equiv of $FeCl_3$. The results in the five-ring series, **17**, are collected in Table 3. In keeping with previous experience, cyclization to form the [3.3.0] system required several hours at room temperature and proceeded in modest yields. The ratios of stereoisomeric *cis*-ring-fused products were determined by capillary GC. Determination of the stereostructure was achieved by hydrogenation of the **19e** mixture to the known[25] saturated ketones (H_2-**19**). The major component was assigned as the (*C,T*)-isomer by comparison of ^{13}C-NMR data for this compound with those reported by Whitesell. Of particular relevance is the chemical shift of the methyl group which is reported at 18.6 ppm. We observed 18.55 ppm for the major component and 14.26 ppm for the minor. The general upfield trend for *endo*-oriented methyl groups was also

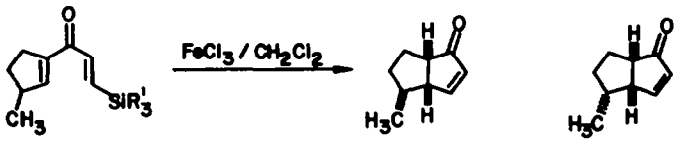


Scheme 7.



Scheme 8.

Table 3. Nazarov cyclizations of **17a–e**



17 (C,T)-**19** (C,C)-**19**

Substrate	R′	Time (h)	Temp (°)[a]	(*C*,*T*)	(*C*,*C*)	Yield (%)
17a	Me_3Si	2.5	20	54	46	50
17b	Me_2PhSi	3	20	59	41	46
17c	$MePh_2Si$	2	20	62	38	41
17d	Ph_3Si	4	20	76	24	13
17e	i-Pr_3Si	4	20	79	21	13

[a] Reactions were initiated at 0° for 30 min then warmed to room temperature.

manifest in the enones **19** (major: 20.05 ppm; minor: 15.03 ppm).

The stereocontrol was disappointing, although increasing the bulk of the silicon substituents did improve the diastereoselectivity in the expected direction albeit in unacceptable yields. The predominent product arises from attack on the sterically less-hindered face of the internal olefin. The diminished influence of the remote methyl group in directing the conrotation may be due to its disposition away from the bond-forming center. Figure 1 illustrates this point. The projection of the C(3′)—CH_3 bond on the C(5′)—C(1′)—C(2′)—C(3′) plane deviates 17.5° from being parallel to the internal olefin. Consequently the methyl group points away and is less able to bias the approach of the vinylsilane sterically.

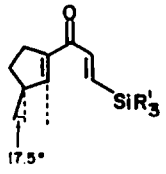
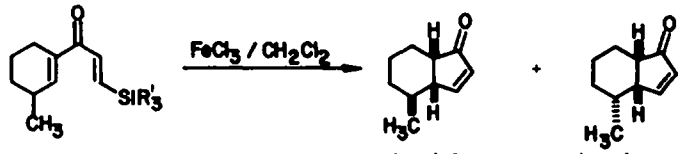


Fig. 1.

The results for cyclization in the six-ring series **18** are collected in Table 4. Compared to **18a**, all phenyl-substituted systems react more slowly, and with the exception of **18d** the yields were all good. The chromatographic analyses and structure assignments for **20** have been discussed previously. There is an incremental increase in the diastereoselectivity through the phenyl series, but the best selectivity was observed for **18e**. The success of **18b** has additional implications for more complex vinylsilanes which may be accessible using Fleming's silylcupration technology.[26] Further, the good yield obtained for **18c** and the stereoselectivity may be parlayed into an ideal group such as isopropyldiphenyl- or t-butyldiphenylsilyl. Together with the results in the previous section one can expect excellent stereocontrol with substituents larger than methyl using a phenyl-substituted silane.

In summary, the stereoselectivity of the silicon-directed Nazarov cyclization is significantly influenced by the bulk of remote substituents, and the stereochemical outcome is predictable based on the previously proposed model of steric approach control. The stereoselectivity is only slightly influenced by the bulk of the groups on silicon. Remote stereocontrol in five-membered ring systems bearing a methyl substituent was found to be modest.

Table 4. Nazarov cyclization of **18b–e**



18 (C,T)-**6** (C,C)-**6**

Substrate	R′	Time (h)	Temp (°)[a]	(*C*,*T*)	(*C*,*C*)	Yield (%)
5a	Me_3Si	4	0	78	22	99
18b	Me_2PhSi	2	20	84	16	63
18c	$MePh_2Si$	2	20	86	14	83
18d	Ph_3Si	2	20	87	13	15
18e	i-Pr_3Si	4	20	90	10	70

[a] Reactions were initiated at 0° for 30 min then warmed to room temperature for **b–e**.

EXPERIMENTAL

A. *General.* M.ps were determined on a Thomas–Hoover capillary apparatus and are corrected. Bulb-to-bulb distillations were performed on a Buchi GKR-50 Kugelrohr; b.ps refer to air bath temps and are uncorrected. R_f data (Merck, silica gel) are given in the following solvent systems: hexane–EtOAc (H–EA), Me_2CO–C_6H_6 (A–B), hexane (H) or Et_2O (Et). Column chromatography was performed by the method of Still *et al.*[27] (32–64 μm silica gel, Woelm). Analytical GC was performed on a Varian 3700 gas chromatograph fitted with FID. Retention times (T_r) and integrals were obtained from a Hewlett-Packard 3390 recorder [N_2 carrier gas for packed columns (30 ml min^{-1}), H_2 for capillary columns (1 ml min^{-1}), split ratio 30:1]. Columns: (A) WCOT OV-1 (50 m × 0.2 mm); (B) WCOT OV-17 (500 m × 0.2 mm). Analytical HPLC was performed on a Perkin–Elmer Series 1 chromatograph with a Perkin–Elmer LC-75 detector. Columns: ¶(C) 25 mm × 10 mm SiO_2 (5 μm). IR spectra were obtained on either a Perkin–Elmer 1320 or an IBM IR 32 in $CHCl_3$ or CCl_4 soln, respectively, unless otherwise noted. Peaks are reported in cm^{-1}. ^{1}H-NMR spectra were recorded on either Varian EM-390 (90 MHz), Varian XL-200 (200 MHz), or Nicolet NT-360 (360 MHz) spectrometers in $CDCl_3$ with $CHCl_3$ (7.26 δ) or TMS (0.00) as internal standards. Chemical shifts are reported in ppm (δ). Coupling constants (J) are given in Hz. Mass spectra were obtained on a Finnigan MAT CH-5 or a MAT-731 instrument. Data are reported in the form *m/z* (intensity relative to base = 100). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory. THF, Et_2O and DME were distilled from sodium benzophenone. CH_2Cl_2, $(CH_2Cl)_2$, C_6H_6, toluene, hexane and TMEDA were distilled from CaH_2. MeOH was distilled from $Mg(OMe)_2$. All reactions were performed in oven (140°) or flame-dried glassware under N_2.

B. *Starting materials.* The following compounds were prepared by literature methods: **5a**,[16b] **7b–e**,[21] **13**,[28,29] **14**,[30] **18a,e**,[16c] *E*-(2-bromoethenyl)trimethylsilane,[31] *E*-3-trimethylsilylpropenal (**11**),[32] *E*-2-(triisopropylsilylethenyl)tributylstannane,[16c] 3-bromo-2-cyclohexen-1-one.[33]

C. *Preparation of divinyl ketones,* **5b–e**

C.1. *Divinyl carbinols* **6**—*General procedure.* Mg chips (1.8 equiv) and dry THF (1 ml/0.1 g Mg) were placed in a 3-necked flask fitted with condenser, addition funnel and magnetic stir bar. A soln of *E*-2-(bromoethenyl)trimethylsilane (1.8 equiv) in dry THF (8 ml/g bromide) was added to the suspension over 0.5 h. After complete addition the mixture was refluxed for 1 h. The resulting soln was cooled to −30° and a soln of the enal **7** (1.0 equiv) in dry THF (10 ml/g enal) was delivered dropwise through the addition funnel. The reaction was monitored by TLC and when completed, warmed to 0° and quenched with 4% NH_4Cl aq 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 (35 ml/g bromide). The combined Et_2O layers were dried (K_2CO_3) and evaporated to afford a crude product which was chromatographed on silica gel. The divinyl carbinols are fully characterized compounds, but due to space limitations the spectroscopic and physical data will not be given here.

C.2. *Oxidation with* NiO_2—*General procedure.* A stirred soln of the divinyl carbinol (**8b, 8e, 15a–d, 16a–d**) in dry Et_2O (0.1 M) was cooled to 0° and treated with 1.8 equiv of NiO_2. The mixture was warmed to room temp after 30 min and the progress monitored by TLC. To workup, the NiO_2 was filtered off with Celite and washed repeatedly with Et_2O and Me_2CO. After concentration the ketone was chromatographed and distilled.

C.3. *Oxidation with* $BaMnO_4$—*General procedure.* A stirred soln of the divinyl carbinol (**8a,d,f**) in dry CH_2Cl_2 (0.25 M) was cooled to 0° and treated with 10 equiv of $BaMnO_4$. The mixture was warmed to room temp and the progress monitored by TLC. Workup (with CH_2Cl_2) and purification was performed as indicated above.

E - 1 - (3' - *Ethenyl* - 1' - *cyclohexenyl*) - 3 - *trimethylsilyl* - 2 - *propen* - 1 - *one* (**5b**). Yield† 42%, b.p. 105°/0.15 Torr. R_f 0.31 (H–EA, 12:1). IR (film): 2950s, 1650s, 1585m, 990s, 915m. ^{1}H-NMR (360 MHz): 7.12 (d, J = 18.6, 1H), 7.02 (d, J = 18.6, 1H), 6.76 (m, 1H), 5.80–5.79 (m, 1H), 5.10–5.04 (m, 2H), 3.03 (br, 1H), 2.33–2.74 (m, 2H), 1.86–1.41 (m, 4H), 014 (s, 9H). MS (70 eV): 234 (5, M^+), 219 (10), 91 (16), 73 (100). (Found: C, 71.41; H, 9.43. Calc for $C_{14}H_{22}OSi$ (234.38): C, 71.74; H, 9.45%.)

E - 1 - (3' - *Phenyl* - 1' - *cyclohexenyl*) - 3 - *trimethylsilyl* - 2 - *propen* - 1 - *one* (**5c**). Yield† 76%, b.p. 180°/0.01 Torr. R_f 0.51 (H–EA, 4:1). IR (CCl_4): 2942m, 1655s, 1585m, 993m. ^{1}H-NMR (200 MHz): 7.41–7.20 (m, 5H), 7.20 (d, J = 18.2, 1H), 7.05 (d, J = 18.2, 1H), 6.94 (d, J = 1.3, 1H), 3.68–3.62 (m, 1H), 2.44–2.41 (m, 2H), 2.13–1.55 (m, 4H), 0.14 (s, 9H). MS (70 eV): 284 (36, M^+), 269 (18), 157 (99), 91 (76), 73 (100). (Found: C, 75.35; H, 8.45. Calc for $C_{18}H_{24}OSi$ (284.45): C, 76.00; H, 8.50%.)

E - 1 - (3' - t-*Butyl* - 1' - *cyclohexenyl*) - 3 - *trimethylsilyl* - 2 - *propen* - 1 - *one* (**5d**). Yield† 51%, b.p. 100°/0.05 Torr. R_f 0.34 (H–EA, 15:1). IR ($CHCl_3$): 2960s, 1640m, 1630m, 1580w, 860s. ^{1}H-NMR (360 MHz): 7.18 (d, J = 18.8, 1H), 6.87 (d, J = 18.9, 1H), 6.73 (t, J = 4.2, 1H), 2.99–2.97 (br m, 1H), 2.27 (m, 2H), 1.98–1.90 (m, 2H), 1.68–1.58 (m, 2H), 0.95 (s, 9H), 0.25 (s, 9H). MS (70 eV): 264 (0.7, M^+), 208 (38), 135 (39), 118 (53), 73 (100). (Found: C, 72.56; H, 10.73. Calc for $C_{16}H_{28}OSi$ (264.49): C, 72.66; H, 10.67%.)

E - 1 - (3' - *Benzyloxymethoxymethyl* - 1' - *cyclohexenyl*) - 3 - *trimethylsilyl* - 2 - *propen* - 1 - *one* (**5e**). Yield† 86%, b.p. 170°/0.05 Torr. R_f 0.53 (H–EA, 3:1). IR (film): 2950m, 1650s, 1580m, 1250s, 990s. ^{1}H-NMR (90 MHz): 7.40 (s, 5H), 7.10 (s, 2H), 6.93–6.80 (m, 1H), 4.87 (s, 2H), 4.68 (s, 2H), 3.65 (d, J = 6.0, 2H), 2.90–2.53 (m, 1H), 2.52–2.23 (m, 2H), 2.07–1.00 (br m, 4H), 0.27 (s, 9H). (Found: C, 70.74; H, 8.50. Calc for $C_{21}H_{30}O_3Si$ (358.56): C, 70.35; H, 8.43%.)

D. *Preparation of divinyl ketone* **5f**

1 - *Benzyloxy* - 3 - *bromo* - 2 - *cyclohexane* (**10**). A soln of 3 - bromo - 2 - cyclohexen - 1 - one (1.004 g, 5.74 mmol) in 12 ml of dry THF was cooled to −78° and treated with 6.31 ml of a 1.0 M soln of DiBAL–H in CH_2Cl_2. After 30 min at −78° the reaction was quenched with 2 ml of CH_3OH, allowed to warm to 0°, and neutralized with 10 ml of 1 N HCl soln. The mixture was poured into 60 ml of H_2O and extracted with Et_2O (2 × 30 ml, 1 × 60 ml). The individual Et_2O extracts were washed with H_2O and brine (1 × 45 ml each), combined, dried (K_2CO_3) and evaporated. The crude product was bulb-to-bulb distilled to afford 0.974 g of **9** as a clear, colorless oil. Yield 94%, b.p. 85–90%/1.5 Torr, R_f 0.2 (H–EA, 3:1). IR (film): 3300s, 2920s, 1630w, 950s. ^{1}H-NMR (90 MHz): 5.9 (m, 1H), 4.0 (m, 1H), 2.3 (m, 2H), 2.0–1.4 (m, 5H). A 15 ml, 3-necked flask fitted with N_2 inlet, septum and addition funnel was charged with 50% NaH dispersion (0.38 g, 7.92 mmol). The dispersion was washed with dry hexane (3 × 3 ml), covered with 5 ml of dry THF and cooled to 0°. A soln of **9** (0.946 g, 5.31 mmol) in 5 ml of dry THF was added and the resulting orange soln was warmed to room temp then cooled down to 0°. Benzyl bromide (0.63 ml, 531 mmol) and n-$Bu_4N^+I^-$ (0.20 g, 0.53 mmol) were added and the mixture was allowed to warm to room temp. After 4 h the milky mixture was poured onto 50 ml of H_2O and extracted with Et_2O (3 × 25 ml). The Et_2O extracts were washed with H_2O (2 × 25 ml) and brine (1 × 25 ml), dried (K_2CO_3) and evaporated to yield a crude product which was bulb-to-bulb distilled to afford 1.179 g of **10** as a clear, colorless oil. Yield 83%, b.p. 110°/0.13 Torr, R_f 0.23 (H–EA, 12:1). IR ($CHCl_3$): 3010s, 2950s, 1645m, 1455s, 1085s. ^{1}H-NMR (360 MHz): 7.35–7.27 (m, 5H), 6.23–6.21 (m, 1H), 4.56 (s, 2H), 3.98–3.96 (m, 1H), 2.49–2.39 (m, 2H), 1.95–1.64 (m, 4H). MS (70 eV): 187 (12), 177 (13), 91 (100). (Found: C, 58.26; H, 5.86; Br, 30.03. Calc for $C_{13}H_{15}Br$ (267.18): C, 58.44; H, 5.66; Br, 29.91%.)

A soln of **10** (0.559 g, 2.09 mmol) in 20 ml of dry THF was cooled to −78° and treated with 2.4 ml (4.42 mmol) of a 1.82 M soln of t-BuLi in pentane. After 30 min at −78° the bromide

† The yield is for both steps.

was consumed (GC analysis) and a soln of *E*-3-trimethylsilyl-2-propenal (0.351 g, 2.74 mmol) in 2 ml of dry THF was added. The soln was stirred for 15 min at −78° then warmed to 0° and quenched by the addition of 26 ml of 4% NH_4Cl soln. The mixture was extracted with Et_2O (3 × 45 ml) and the Et_2O extracts washed with H_2O (2 × 30 ml) and brine (1 × 30 ml). The combined Et_2O extracts were dried (K_2CO_3) and evaporated to provide a yellow oil which was purified by column chromatography to afford 0.406 g (61%) of **8f** as a clear, colorless oil. The divinyl carbinol (0.329 g, 1.04 mmol) was oxidized with $BaMnO_4$ as described in C.2 to afford 0.239 g of **5f** as a clear, colorless oil. Yield 73%, R_f 0.39 (H–EA, 6:1). IR (CCl_4): 3033m, 2952s, 1655s, 1585m, 1250s, 1088s. ^{1}H-NMR (200 MHz): 7.40–7.34 (m, 5H), 7.16 (d, J = 18.8, 1H), 7.04 (d, J = 18.8, 1H), 6.82 (d, J = 2.3, 1H), 4.73 (d, J = 11.7, 1H), 4.61 (d, J = 11.7, 1H), 4.23 (br m, 1H), 2.32–1.50 (m, 6H), 0.17 (s, 9H). MS (70 eV) 314 (M^+, 0.6), 223 (14), 91 (100), 73 (60). (Found: C, 72.18; H, 8.45; Si, 8.72. Calc for $C_{19}H_{26}O_2Si$ (314.54): C, 72.56; H, 8.33; Si, 8.93%.)

E. *Preparation of alkynylsilanes* (**19**)

General procedure. Mg (3.6 g, 148 mmol) was covered with 12 ml of dry THF in a 100 ml, 3-necked, round-bottomed flask fitted with a reflux condenser, addition funnel, stopper and N_2 inlet. A small crystal of I_2 was introduced. EtBr (16.14 g, 148 mmol) in 12 ml of dry THF was added dropwise and the mixture was refluxed for 1 h after complete addition. A sat soln of acetylene in 120 ml of dry THF was prepared in a 3-necked, round-bottomed flask by bubbling acetylene (passed through, in series, a −78° cold trap, conc H_2SO_4, and K_2CO_3 tower) into the THF at room temp then cooling to 0°. The EtMgBr was added to the acetylene soln in six portions via syringe and then the mixture was warmed to room temp. Introduction of acetylene was continued as the appropriate chlorosilane (125 mmol, neat) was added. After complete addition the acetylene flow was halted and the mixture was heated to reflux for 36 h. Progress could be monitored by GC analysis of small aliquots. The flask was cooled to 0° and the reaction quenched by careful addition of 110 ml of H_2O. The resulting soln was extracted with Et_2O (2 × 220 ml) and the individual extracts were washed with H_2O (1 × 220 ml) and brine (1 × 220 ml), combined, dried ($MgSO_4$) and concentrated. The crude product was filtered through a plug of SiO_2 (hexane eluant to remove any silanol). The filtrate was concentrated and distilled (**19d** was also chromatographed).

Dimethylethynylphenylsilane (**19b**). Yield 86%, b.p. 100°/6 Torr, R_f 0.25 (H). IR (CCl_4): 3293s, 2037s, 1429s, 1119. ^{1}H-NMR (200 MHz): 7.79–7.75 (m, 2H), 7.51–7.48 (m, 3H), 2.62 (br s, 1H), 0.57 (s, 6H). MS (70 eV): 160 (M^+, 22), 146 (15), 145 (100).

Diphenylethynylmethylsilane (**19c**). Yield 85%, b.p. 150°/1 Torr, R_f 0.15 (H). IR ($CHCl_3$): 3290s, 2040s, 1430s, 1113s. ^{1}H-NMR (200 MHz): 7.67–7.62 (m, 4H), 7.38–7.31 (m, 6H), 2.56 (s, 1H), 0.70 (s, 3H). MS (70 eV): 222 (M^+, 21), 207 (100), 145 (11). (Found: C, 80.82; H, 6.35. Calc for $C_{15}H_{14}Si$ (222.32): C, 81.02; H, 6.35%.)

Ethynyltriphenylsilane (**19d**). Yield 51%, b.p. 160°/0.3 Torr, m.p. 33.5–35.0°, R_f 0.11 (H). IR (CCl_4): 3293s, 2039m, 1429s, 1115s. ^{1}H-NMR (200 MHz): 7.8–7.3 (m, 15H), 2.70 (s, 1H). MS (70 eV): 285 ($M^+ + 1$, 17), 284 (M^+, 63), 207 (100), 181 (45), 105 (37). (Found: C, 84.07; H, 5.76. Calc for $C_{20}H_{16}Si$ (284.39): C, 84.46; H, 5.67%.)

F. *Preparation of silylethenylstannanes*, **12**

General procedure. A neat soln of freshly distilled n-Bu_3SnH (5.24 g, 18 mmol) and the appropriate alkynylsilane (18 mmol) was heated to 115–120° in a 50 ml flask equipped with a thermometer and N_2 inlet. The progress of the reaction was monitored by GC and TLC, and the product was distilled directly (**12d** was chromatographed as well).

E-2-(*Dimethylphenylethenyl*)*tributylstannane* (**12b**). Yield 88%, b.p. 160°/0.6 Torr. IR (CCl_4): 3071w, 2959s, 1012m. ^{1}H-NMR (200 MHz): 7.63–7.40 (m, 5H), 7.22 (d, J = 22.7, 1H), 6.83 (d, J = 22.7, 1H), 1.7–0.85 (m, 27H), 0.42 (s, 6H). MS (70 eV): 396 (11), 395 (46), 394 (20), 393 (35), 392 (14), 391 (18), 135 (100). $C_{21}H_{40}SiSn$ (439.39).

E-2-(Diphenylmethylsilylethenyl)tributylstannane (**12c**). Yield 90%, b.p. 180°/0.03 Torr. IR ($CHCl_3$): 2965s, 2930s, 1465m, 1110s. ^{1}H-NMR (90 MHz): 7.6–7.2 (m, 11H), 6.98 (d, J = 10, 1H), 1.8–0.8 (m, 27H), 0.64 (s, 3H). MS (70 eV): 458 (14), 457 (48), 456 (37), 454 (6), 453 (19), 197 (100). (Found: C, 62.86; H, 8.17; Sn, 23.17. Calc for $C_{27}H_{42}SiSn$ (513.41): C, 63.17; H, 8.25; Sn, 23.11%.)

E-2-(*Triphenylsilylethenyl*)*tributylstannane* (**12d**). Yield 65°, b.p. 220°/0.3 Torr, R_f 0.22 (H). IR ($CHCl_3$): 3070m, 2960s, 1429m, 1110s. ^{1}H-NMR (90 MHz): 7.6–7.1 (m, 17H), 2.0–0.7 (m, 27H). MS (70 eV): 520 (11), 519 (34), 518 (16), 517 (25), 515 (13), 259 (100). (Found: C, 66.65; H, 7.78; Sn, 20.43. Calc for $C_{32}H_{44}SiSn$ (575.54): C, 66.79; H, 7.71; Sn, 20.62%.)

G. *Preparation of divinyl ketone* **17**, **18** *from enals* **13**, **14**

G.1. *Divinyl carbinols* **15**, **16**. A soln of the appropriate stannane, **12b–d** (1.1 equiv) in dry THF (3.1 ml/mmol enal) in a 3-necked flask fitted with N_2 inlet, septum and thermometer was cooled to −78°. n-BuLi in hexane was added dropwise at −78° until the stannane was consumed as indicated by GC analysis. The soln was taken through a warming cycle to −20° for 20 min then recooled to −78°. A soln of the appropriate enal, **13–15** (1 equiv/equiv n-BuLi) in dry THF (0.44 ml/mmol enal) was added dropwise, keeping the temp near −78°. After complete addition the flask was warmed to 0° and the reaction quenched with H_2O (4.4 ml/mmol enal). The mixture was extracted with Et_2O (3 × 9 ml/mmol enal), the individual extracts were washed with equal vols of H_2O and brine. The Et_2O extracts were combined, dried (K_2CO_3) and concentrated to afford a crude product which was purified by chromatography on silica gel. The divinyl carbinols are fully characterized compounds, but due to space limitations the spectroscopic and physical data will not be given here.

G.2. *Divinyl ketones*, **17**, **18**—*General procedure.* The purified divinyl carbinols were oxidized with NiO_2 as described in C.2, and the products purified by column chromatography and distillation. All of the following derivatives have been fully characterized (^{1}H-NMR, IR, MS, C, H) but only the ^{1}H-NMR data are given here due to space limitations.

E-1-(3′-*Methyl*-1′-*cyclopentenyl*)-3-*trimethylsilyl*-2-*propen*-1-*one* (**17a**). Yield† 60%, b.p. 75°/0.04 Torr, R_f 0.48 (H–EA, 6:1). ^{1}H-NMR (200 MHz): 7.13 (d, J = 18.7, 1H), 7.01 (d, J = 8.7, 1H), 6.68 (d, J = 1.6, 1H), 3.02–2.94 (m, 1H), 2.70–2.44 (m, 2H), 2.24–2.08 (m, 1H), 1.52–1.36 (m, 1H), 1.12 (d, J = 7.0, 3H), 0.14 (s, 9H).

E-1-(3′-*Methyl*-1′-*cyclopentenyl*)-3-*dimethylphenylsilyl*-2-*propen*-1-*one* (**17b**). Yield† 56%, b.p. 110°/0.04 Torr, R_f 0.45 (H–EA, 6:1). ^{1}H-NMR (200 MHz): 7.67–7.36 (m, 5H), 7.28 (d, J = 18.6, 1H), 7.06 (d, J = 18.4, 1H), 6.66 (dd, J = 3.8, 1.8, 1H), 3.05–2.94 (m, 1H), 2.74–2.50 (m, 2H), 2.23–2.14 (m, 1H), 1.60–1.47 (m, 1H), 1.14 (d, J = 7.0, 3H), 0.45 (s, 6H).

E-1-(3′-*Methyl*-1′-*cyclopentenyl*)-3-*diphenylmethylsilyl*-2-*propen*-1-*one* (**17c**). Yield† 70%, R_f 0.41 (H–EA, 6:1). ^{1}H-NMR (200 MHz): 7.56–7.48, 7.40–7.31 (2m, 11H), 7.22 (d, J = 18.4, 1H), 6.59 (d, J = 1.9, 1H), 3.00–2.85 (m, 1H), 2.62–2.53 (m, 2H), 2.16–2.09 (m, 1H), 1.49–1.41 (m, 1H), 1.09 (d, J = 7.0, 3H), 0.71 (s, 3H).

E-1-(3′-*Methyl*-1′-*cyclopentenyl*)-3-*triphenylsilyl*-2-*propen*-1-*one* (**17d**). Yield† 73%, b.p. 125°/0.04 Torr, m.p. 98°, R_f 0.39 (H–EA, 6:1). ^{1}H-NMR (200 MHz): 7.11 (s, 2H), 6.67 (dd, J = 3.5, 1.6, 1H), 3.03–2.96 (m, 1H), 2.72–2.55 (m, 2H), 2.27–2.12 (m, 1H), 1.56–1.31 (m, 1H), 1.27–1.00 (m, 21H).

E-1-(3′-*Methyl*-1′-*cyclohexenyl*)-3-*dimethylphenylsilyl*-2-*propen*-1-*one* (**18b**). Yield† 60%, b.p. 140°/0.03 Torr, R_f 0.46 (H–EA, 6:1). ^{1}H-NMR (200 MHz): 7.57–7.35 (m, 5H), 7.23 (d, J = 18.4, 1H), 7.11 (d, J = 18.4, 1H), 6.73 (d, J = 1.6, 1H), 2.42–1.19 (m, 7H), 1.10 (d, J = 7.3, 3H), 0.45 (s, 6H).

E-1-(3′-*Methyl*-1′-*cyclohexenyl*)-3-*diphenylmethylsilyl*-

† The yield is for both steps.

2-*propen*-1-*one* (**18c**). Yield† 70%, R_f 0.43 (H–EA, 6:1). ^{1}H-NMR (200 MHz): 7.56–7.31 (m, 11H), 7.11 (d, J = 18.4, 1H), 6.67 (s, 1H), 2.39–2.18 (m, 3H), 1.83–1.73 (m, 2H), 1.54–1.42 (m, 1H), 1.26–1.10 (m, 1H), 1.05 (d, J = 7.0, 3H), 0.71 (s, 3H).

E-1-(3′-*Methyl*-1′-*cyclohexenyl*)-3-*triphenylsilyl*-2-*propen*-1-*one* (**18d**). Yield† 60%, m.p. 67°, R_f 0.41 (H–EA, 6:1). ^{1}H-NMR (200 MHz): 7.64–7.09 (m, 16H), 7.14 (d, J = 18.4, 1H), 6.63 (s, 1H), 2.50–1.15 (m, 7H), 1.05 (d, J = 7.0, 3H).

H. *Cyclization of divinyl ketones*

General procedure. To a cold (0°) soln of the divinyl ketone in dry CH_2Cl_2 (0.08 M) was added in one portion 1.05 equiv of anhydrous $FeCl_3$. The reactions were monitored by TLC and warmed to room temp if necessary (see Tables 1, 3 and 4 for reaction times and temps). The reaction was quenched by the addition of an equal vol. of brine and dilution with Et_2O (50 ml/g ketone). The H_2O layer was separated, extracted with Et_2O (2 × 50 ml/g ketone) and the individual Et_2O extracts were washed with H_2O and brine (1 × 34 ml/g ketone). The combined organic extracts were dried ($MgSO_4$) and evaporated to afford a crude product which was purified by column chromatography and distillation.

H.1. *Hydrogenation of 2-cyclopentenones—General procedure.* A soln of the enone, **6b–f**, **19**, **20** (10–100 mg) in 5 ml of dist. EtOAc was stirred in an atmosphere of H_2 with 0.01 equiv of 5% Pd/C until H_2 uptake ceased (1–6 h). The mixture was filtered through Celite, with additional EtOAc (2 × 5 ml) and the filtrate was concentrated to give a colorless oil of sufficient purity for equilibration.

H.2. *Base-catalyzed epimerization of ketones—General procedure.* A soln of the sat ketone from H.1 (10 mg) in 1 ml of dist. CH_3OH was treated with 0.05 equiv of a titrated soln of $NaOCH_3$ in CH_3OH. The soln was stirred at room temp and the progress monitored by capillary GC until the ratios were constant.

4β-*and*4α-*Ethenyl*-3aβ,4,5,6,7,7aβ-*hexahydro*-1H-*inden*-2-*en*-1-*one* [(*C,T*)- *and* (*C,C*)-**6b**]. Yield 66%, b.p. 75°/0.03 Torr, R_f 0.27, 0.23 (H–EA, 5:1). GC analysis column B [100° (2 min), 20° min^{-1}, 260° (15 min)]: t_R 9.87 min (*C,T*) and 10.21 min (*C,C*). IR (film): 3070m, 2930s, 1710s, 1580m, 920s. ^{1}H-NMR (360 MHz): 7.74 (dd, J = 5.8, 3.0, 0.7H), 7.63 (dd, J = 5.8, 2.3, 0.3H), 6.23 (dd, J = 5.8, 2.2, 0.3H), 6.15 (dd, J = 5.8, 1.2, 0.7H), 5.91–5.84 (m, 0.3H), 5.80–5.70 (m, 0.7H), 5.14–4.98 (m, 2H), 2.72–2.67 (m, 0.7H), 2.67–2.61 (m, 0.3H), 2.52 (d, J = 11.7, 6.2, 0.3H), 2.42 (dd, J = 12.9, 6.2, 0.7H), 2.03–1.13 (m, 6H). MS (70 eV): 162 (M^+, 24), 91 (49), 82 (100). (Found: C, 81.17; H, 8.54. Calc for $C_{11}H_{14}O$ (162.21): C, 81.44; H, 8.69%.) This mixture was hydrogenated as described in H.2. Yield 90%. GC analysis column B (150° isothermal): t_R 13.09 min (68.7%), 13.66 min (4%) and 14.22 min (27.3%). This mixture was equilibrated as described in H.3 to afford a four-component mixture; GC analysis column B (150° isothermal): t_R 12.86 min [31.4% (*T,T*)-H_2-**6b**], 13.09 min [39.0% (*C,T*)-H_2-**6b**], 13.66 min [3.3% (*T,C*)-H_2-**6b**], 14.22 min [26.4% (*C,C*)-H_2-**6b**].

4β-*Phenyl*-3aβ,4,5,6,7,7aβ-*hexahydro*-1H-*inden*-1-*one* [(*C,T*)-**6c**]. Yield 76%, b.p. 180°/0.1 Torr, m.p. 64–68°, R_f 0.28 (H–EA, 4:1). GC analysis column B (180°, isothermal): t_R 14.6 min [94% (*C,T*)-**6c**], 16.9 min [6% (*C,C*)-**6c**]. IR (CCl_4): 2936m, 1717s, 1653w, 1584w. ^{1}H-NMR (200 MHz): 7.50 (dd, J = 5.8, 3.1, 1H), 7.40–7.20 (m, 5H), 6.17 (dd, J = 5.8, 1.6, 1H), 3.06 (dddd, J = 10.0, 6.3, 3.1, 1.6, 1H), 2.25 (ddd, J = 10.0, 7.4, 5.4, 1H), 2.18–2.08 (m, 2H), 1.85–1.40 (m, 5H). MS (70 eV) 212 (M^+, 47), 130 (100), 95 (90), 91 (30). (Found: C, 84.92; H, 7.70. Calc for $C_{15}H_{16}O$ (212.31): C, 84.87; H, 7.60%.)

4β-t-*Butyl*-3aβ,4,5,6,7,7a-*hexahydro*-1H-*inden*-1-*one* [(*C,T*)-**6d**]. Yield 63%, b.p. 90°/0.03 Torr, m.p. 42–43°, R_f 0.24 (H–EA, 8:1). GC analysis column C (150° isothermal): t_R 16.6 min [94% (*C,T*)-**6d**], 20.2 min [6% (*C,C*)-**6d**]. IR (film): 2950s, 1710s, 1615w, 1060s. ^{1}H-NMR (360 MHz): 7.57 (dd, J = 5.6, 3.2, 1H), 6.18 (dd, J = 5.7, 1.3, 1H), 3.13 (m, 1H), 2.26 (dd, J = 6.3, 1.6, 1H), 2.14 (m, 1H), 1.76 (m, 1H), 1.54 (m, 1H), 1.40–1.30 (m, 4H), 0.93 (s, 9H). MS (70 eV) 192 (M^+, 0.8), 135 (100), 108 (30). (Found: C, 80.91; H, 10.21. Calc for $C_{13}H_{20}O$ (192.28): C, 81.20; H, 10.84%.) This mixture was hydrogenated to give a mixture of ketones; GC analysis column B (150° isothermal): t_R 15.4 min [94% (*T,T*)-H_2-**6d**], 18.0 min (0.6%), 18.2 min [5.0% (*C,C*)-H_2-**6d**]. This mixture was unchanged upon treatment with $NaOCH_3$. Apparently epimerization occurred during hydrogenation.

4β-*Benzyloxy*-3aβ,4,5,6,7,7aβ-*hexahydro*-1H-*inden*-1-*one* [(*C,T*)-**6f**]. Yield 76%, b.p. 150°/0.04 Torr, R_f 0.19 (H–EA, 6:1). HPLC analysis column C (H–i-PrOH 60:1, 3 ml min^{-1}): t_R 15.2 min (90%), 16.4 min (3%), 17.7 min (7%). IR (CCl_4): 2940s, 1715s, 1094. ^{1}H-NMR (200 MHz): 7.84 (dd, J = 5.7, 2.4, 1H), 7.35 (s, 5H), 6.18 (dd, J = 5.7, 1.3, 1H), 4.67 (d, J = 11.8, 1H), 4.44 (d, J = 11.8, 1H), 3.14 (ddd, J = 9.7, 8.5, 2.4, 1.3, 1H), 2.51–2.46 (m, 1H), 1.96–1.55 (m, 6H). MS (70 eV): 242 (M^+, 2), 151 (3), 91 (100). HR-MS: $C_{16}H_{12}O_2$, calc: 242.1307; obs: 242.1312.

4β-*and*4α-*Methyl*-1,3aβ,4,5,6,6aβ-*hexahydropentalen*-1-*one* [(*C,T*)-*and*(*C,C*)-**23**]. B.p. 125°/1.0 Torr, R_f 0.19 (H–EA, 6:1). GC analysis column A (100° isothermal): t_R 15.8 min [(*C,T*)-**23**], 17.2 min [(*C,C*)-**23**]. IR (film): 2957s, 1701s, 1586, 1186s. ^{1}H-NMR (200 MHz): 7.62–7.55 (m), 6.21 (dd, J = 5.5, 1.8), 6.05 (dd, J = 5.6, 1.7), 3.28–3.22 (m), 2.89–2.64 (m), 2.15–1.26 (m), 1.04 (d, J = 7.0), 1.03 (d, J = 7.2). ^{13}C-NMR (50 MHz): (*C,T*)-**23** 167.23, 133.35, 55.16, 49.61, 36.97, 32.21, 27.42, 20.05. (*C,C*)-**23** 165.63, 136.00, 50.44, 50.14, 37.05, 31.49, 29.17, 15.93. MS (70 eV): 136 (M^+, 58), 121 (47), 95 (47), 77 (46), 39 (100). $C_9H_{12}O$ (136.21). This mixture of enones was hydrogenated according to the general procedure H.2 to afford sat ketones with the following data. ^{13}C-NMR (50.2 MHz): (*C,T*)-H_2-**23** 188.55, 77.35, 77.00, 52.37, 49.37, 40.43, 36.49, 35.19, 27.80, 23.87, 18.55. (*C,C*)-H_2-**23** 188.55, 77.19, 76.64, 51.73, 45.06, 39.54, 38.32, 32.38, 28.76, 21.45, 14.26.

4β- and 4α-*Methyl*-3aβ,4,5,6,7,7aβ-*hexahydro*-1H-*inden*-1-*one* [(*C,T*)- *and* (*C,C*)-**20**]. The preparation, characterization and stereochemical assignment of these compounds have been described previously.[16c]

† The yield is for both steps.

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