one, 2737-36-2; *endo-cis*-4,4,8-trimethylbicyclo[3.3.0]octan-2-one, 10067-57-9; *exo-cis*-4,8-dimethylbicyclo[3.3.0]oct-3-en-2-one, 5260-84-4; 2,2,5-trimethylcyclopentanone, 4573-09-5; 2,2,5-trimethylcyclopentanone benzenesulfonylhydrazone, 73839-56-2; 2,3-dibromo-3-(4-methylphenyl)propionic acid, 52916-86-6; *p*-tolyl(trimethylsilyl)acetylene, 4186-14-5; β,β-dimethylacryloyl chloride, 3350-78-5; crotonyl chloride, 10487-71-5; acryloyl chloride, 814-68-6; β-chloropropionyl chloride, 625-36-5.

Silanes in Organic Synthesis. 9. Enesilylation as a Method for 1,2-Carbonyl Migration within Ketones and for Conversion to 1,2-Transposed Allylic Alcohols[1]

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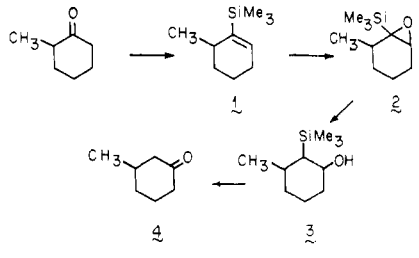
Received April 24, 1980

Vinylsilanes are shown to be valuable synthetic intermediates in useful transformations of ketones. The epoxidation of vinylsilanes followed by lithium aluminum hydride reduction and oxidation with chromic acid and sulfuric acid in a two-phase (ether/water) system often gives high yields of 1,2-transposed ketones. With singlet oxygen and sequential sodium borohydride reduction, 2-trimethylsilyl alcohols are produced in which the α position of the parent ketone has been regiospecifically oxygenated. Fluoride ion promoted desilylation completes the conversion to the migrated allylic alcohol.

The carbonyl group is pivotal in bringing latitude to organic synthesis. The need to relocate this functional group within a molecule occurs with sufficient frequency that interest in efficient methods of carbonyl transposition remains high. Various procedures have been developed for effecting site exchange within saturated[4-13] and α,β-unsaturated ketones,[14-17] sometimes in tandem with an alkylation step,[18-20] and these have met with varying degrees of accepted usage. In this paper, we describe a quite different approach to the 1,2-transposition of ketones which takes advantage of the chemical properties associated with covalently bonded silicon.[21] Also described herein is a simple procedure which shifts the position of a ketone carbonyl in an entirely predictable manner with simultaneous introduction of a double bond.[22] Little known α-silylated allylic alcohols and ketones result, and these substances serve as precursors to the silicon-free end products. The high regioselectivity of these novel functionality-transposing reactions suggests that they may hold considerable importance in organic synthesis.

Scheme I



1,2-Keto Transposition. In the accompanying paper, it was demonstrated that vinyl carbanions, generated through reaction of ketone arenesulfonylhydrazones with alkyllithium reagents in tetramethylethylenediamine solution, react with chlorotrimethylsilane to deliver vinylsilanes in excellent yield. Where relevant, this transformation is regiospecific, deprotonation occurring preferentially for electronic and steric reasons at the less substituted α position. With the introduction of such unsaturation comes the further possibility of functionalizing the carbon atom β to silicon. This phenomenon provides for the possibility of vinylsilane-mediated oxygen transposition.

The methodology envisioned for the 1,2-carbonyl relocation is illustrated in Scheme I. Epoxidation of 1 to give

(1) Part 8: Paquette, L. A.; Fristad, W. E.; Dime, D. S.; Bailey, T. R. *J. Org. Chem.*, accompanying paper in this issue.
(2) The Ohio State University Graduate (1975-1976) and Dissertation Fellow (1978-1979).
(3) Undergraduate research participant, 1976-1978.
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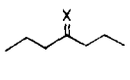
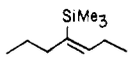
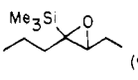
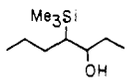
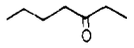
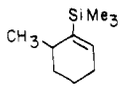
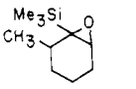
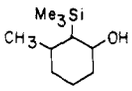
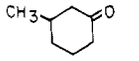
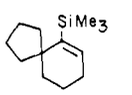
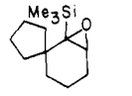
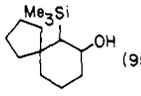
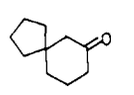
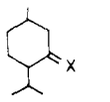
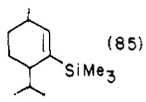
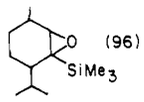
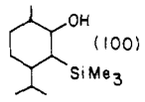
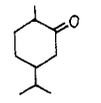
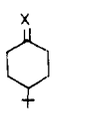
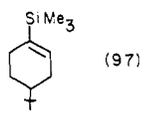
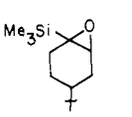
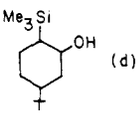
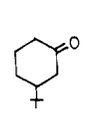
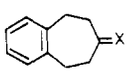
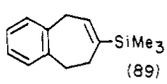
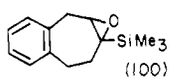
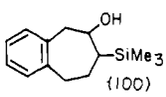
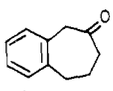
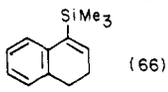
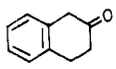
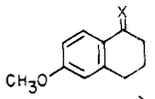
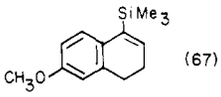
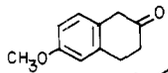
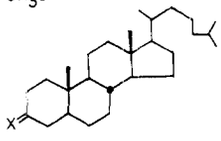
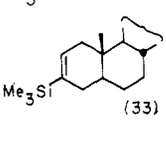
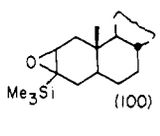
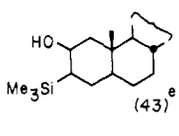
Table I. 1,2-Carbonyl Transposition Data[a]

substrate[b]	vinylsilane	epoxysilane	β-silyl alcohol	ketone
	 (96)	 (97.5)	 (88)	 (84)
	 (91)	 (89)	 (83)	 (84)
	 (67)	 (91)	 (95)	 (66)
	 (85)	 (96)	 (100)	 (90)
	 (97)	 (87)	 (d)	 (83)
	 (89)	 (100)	 (100)	 (63)
	 (66)	c	c	 (83)
	 (67)	c	c	 (96)
	 (33)	 (100)	 (43)[e]	(87)

[a] The percentage yields which are provided in parentheses represent the isolated yields at each step. [b] For convenience purposes, these structures will be further defined as follows: a, X = O; b, X = $NNHSO_2C_6H_5$. [c] These intermediates were not isolated under the conditions employed (see text). [d] See text for discussion. [e] The remainder of the product was the α-silyl alcohol.

epoxysilane **2** is followed by hydride reduction which proceeds with cleavage of the α-carbon–oxygen bond.[23] Oxidation of the resulting β-silyl alcohol (**3**) and hydrolytic desiliconation delivers the new ketone **4**.

The epoxidation of various vinylsilanes was found to be a smooth process when conducted at 0 °C in buffered dichloromethane solution with 1.1 equiv of *m*-chloroperbenzoic acid. While the rate of epoxidation of vinylsilanes is slower than that of similarly alkyl substituted olefins, the reaction, conveniently monitored by thin-layer chromatography, requires but 0.5–2 h. These results (Table I) conform to earlier studies of vinylsilane epoxidation.[24] The epoxysilanes themselves are capable of further reaction when 2 equiv of *m*-chloroperbenzoic acid is used or the buffer is omitted. In these cases, the epoxides appear to undergo ring opening with *m*-chlorobenzoate anion with resultant formation of high-molecular-weight products which were not further investigated.

With several of the vinylsilanes studied, production of a pair of stereoisomers was possible. The first such example is **1** which was presumed to exist as a pair of rapidly equilibrating conformational isomers.[25] In actuality, the isomeric epoxides **5** and **6** were formed in a ratio of 38:62. The two products were separated by preparative gas-phase chromatography and identified by $Eu(fod)_3$ shifting of their

Table II. Lanthanide-Induced Shifting ($CDCl_3$ Solution, 90 MHz)

compd	signal	amt $Eu(fod)_3$, mol %	δ	ΔEu, ppm	slope, Δδ/Δmol %
5	α-epoxy H	0	2.80	21	0.21
		12.8	5.00		
		20.1	6.41		
		28.8	9.09		
	3-CH_3	0	0.82	8.5	0.085
		12.8	1.70		
		20.1	2.25		
		28.8	3.32		
6	α-epoxy H	0	2.75	19	0.19
		19.7	5.86		
		25.0	7.58		
		42.3	10.58		
	3-CH_3	0	0.88	4.8	0.048
		25.0	2.13		
		42.3	2.89		

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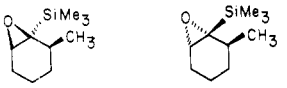
(24) (a) Bižant, V.; Matoušek, V. *Collect. Czech. Chem. Commun.* **1958**, *24*, 3758. (b) Plueddeman, E. P.; Fanger, G. *J. Am. Chem. Soc.* **1959**, *81*, 2632. (c) Sakurai, H.; Hayashi, N.; Kumada, M. *J. Organomet. Chem.* **1969**, *18*, 351. (d) Eisch, J. J.; Trainor, J. T. *J. Org. Chem.* **1963**, *28*, 487.

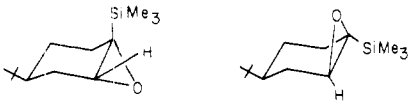
(25) For a detailed discussion of the various parameters at work, consult: Rickborn, B.; Lwo, S.-Y. *J. Org. Chem.* **1965**, *30*, 2212.



5 6

^{1}H NMR spectra (Table II).

1-(Trimethylsilyl)-4-*tert*-butylcyclohexene, while probably existing overwhelmingly in a single conformation, offers no obviously less hindered face at its π bond. In line with this analysis, the ^{1}H NMR spectrum of its epoxidation mixture was found to exhibit two signals for protons on an epoxide ring near δ 3.0 in an approximate ratio of 60:40. The major downfield signal is considered to correspond to **7** which has its >CHO proton locked in a quasi-equa-



7 8

torial position. The minor isomer should then be represented by the cisoid structure **8** if the usual rule of chemical shifts concerning axial/equatorial cyclohexyl hydrogens is obeyed. Normally, axial hydrogens resonate at higher field than otherwise equivalent equatorial hydrogens. These assignments were subsequently corroborated by hydride reduction (see below).

3-(Trimethylsilyl)-2-cholestene gave a single epoxide. Since the trimethylsilyl group places no new steric demands on the steroidal nucleus, the epoxidation was assumed to proceed from the α face as was known in the parent hydrocarbon[26] as well as in 3-methylcholest-2-ene.[27]

The key principle on which the 1,2-keto transposition rests is the regioselective hydride ring opening to give β-hydroxysilanes. This pathway has previously been established by Eisch and Trainor for a triphenylvinylsilane epoxide.[23a] In this simple system, however, regiospecificity was noted intriguingly to fall off with increasing amounts of lithium aluminum hydride. More recently, Robbins and Whitman demonstrated that comparable hydride reduction of the conformationally flexible 1,2-epoxy-1-(trimethylsilyl)cyclohexane also gave cleavage of the α-carbon–oxygen bond.[23b] In addition, this reduction proved to be stereospecific, with *cis*-2-(trimethylsilyl)cyclohexanol being the sole product.

In the present study, the epoxysilane reductions were carried out with lithium aluminum hydride in ether at room temperature (first three entries in Table I) or at reflux (the benzocycloheptyl example). The menthane derivative (fourth table entry) was successfully reduced in refluxing tetrahydrofuran. In all of the above acyclic or conformationally flexible ring cases, the epoxysilane was cleanly opened to the β-silyl alcohol. However, the electronic directing effect of silicon proved inadequate to overcome the normal kinetic bias for trans diaxial opening in conformationally rigid systems. Thus, the 4-*tert*-butylcyclohexyl system gave a mixture of products (Table III) and the cholestanyl derivative underwent exclusively the trans diaxial opening process exhibited by its all-carbon counterpart.[27] It is, of course, not feasible to estimate accurately the ground- and transition-state conformational interaction energies which gain importance within **7** and **8** as reduction proceeds. Nor can some degree of anomalous mechanistic behavior be ruled out in such reactions.[28]

(26) Malunowica, I.; Fajkoš, J.; Šorm, F. *Chem. Listy* **1958**, *52*, 2359.
(27) Barton, D. H. R.; Campos-Neres, A. S.; Cookson, R. C. *J. Chem. Soc.* **1956**, 3500.

Table III. Specificity of Mixed-Hydride Reductions of 7/8 (60:40)[a,b]

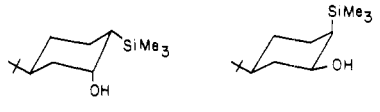
$LiAlH_4$/$AlCl_3$	probable effective reagent	9	10	11	12
1:0	$LiAlH_4$	76		24	
1:1	AlH_2Cl	5		64	31
2:1	AlH_2Cl + AlH_3	9		50	41
3:1	AlH_3	11		57	32

[a] Reactions conducted in anhydrous ether at 0 °C to room temperature. The percentage values given were obtained by vapor-phase chromatography (thermal conductivity detector), are uncorrected as to relative response to detection, and are normalized to exclude small amounts of recovered epoxide. [b] Structural assignments to these alcohols were made chiefly on the basis of their ^{1}H NMR spectra (Musker, W. K.; Larson, G. L. *Tetrahedron Lett.* **1968**, 3481).

However, the levels at which **9** and **10** were produced were clearly not at all acceptable for synthetic purposes.

As a means of enhancing the electrophilic nature of the α carbon in such epoxides, the efficacy of various "mixed hydrides"[29] was examined. A remarkably enhanced specificity for α attack, particularly with AlH_2Cl (95% combined yield of **11** and **12**), was uncovered. Application of similar methodology to the cholestanyl epoxide likewise resulted in higher levels of α-bond fission, thereby illustrating the versatility of this modification.

The stereochemistry of **11** and **12** was established on several grounds. The fact that **11** was the only β-silyl

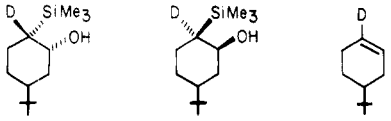


11 12

alcohol formed upon $LiAlH_4$ reduction was construed as adequate proof that the hydroxyl group is axial. On this basis, the new β-silyl alcohol found in the mixed hydride reductions must be the equatorial isomer **12**. These assignments are supported by ^{1}H NMR chemical shift data, the axial CHOH of **12** being located 0.25 ppm to higher field than the related equatorial proton in **11**.

To dismiss the possibility that these reductions were not complicated by prior rearrangement of the epoxysilanes to β-trimethylsilyl ketones,[30] the **7**/**8** mixture was reduced with a mixed hydride prepared with lithium aluminum deuteride. If the products are to result from carbonyl reduction, then a deuterium must be positioned β to the trimethylsilyl group. If, however, the epoxide is reduced directly, the α position will be isotopically labeled. Both β-trimethylsilyl alcohols gave evidence of containing deuterium exclusively α to silicon as in **13** and **14** (^{1}H NMR integration and mass spectral analysis). Additionally, treatment of **13** with sodium hydride in refluxing tetrahydrofuran caused elimination of trimethylsilanoxide and afforded 4-*tert*-butylcyclohexene-*1-d* (**15**).

(28) (a) Rickborn, B.; Quartucci, J. *J. Org. Chem.* **1964**, *29*, 3185. (b) Rickborn, B.; Lambe, W. E., II. *Ibid.* **1967**, *32*, 537. (c) Murphy, D. K.; Alumbaugh, R. L.; Rickborn, B. *J. Am. Chem. Soc.* **1969**, *91*, 2649.
(29) Rerick, M. N.; Eliel, E. L. *J. Am. Chem. Soc.* **1962**, *84*, 2356 and earlier papers in this series.
(30) For examples of this rearrangement, see: (a) Obayashi, M.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1977**, 1807; (b) Obayashi, M.; Utimoto, K.; Nozaki, H. *Ibid.* **1978**, 1383; (c) Hudrlik, P. F., et al. *Ibid.* **1976**, 1453; (d) reference 23c.



13 14 15

Oxidation and desilylation of the β-silyl alcohols would complete the ketone transposition. While a variety of oxidative conditions desilylated the initially formed product to varying degrees,[31-33] treatment with a stoichiometric quantity of chromic acid and 10 molar equiv of sulfuric acid in a two-phase system (ether–water) proved routinely successful in delivering the pure transposed ketone. Under these protic conditions, the intermediate β-silyl ketones suffered efficient carbon–silicon bond cleavage. Oxidation yields of greater than 80% were achieved with this modification of the original Brown procedure.[34]

The best oxidation procedure we have uncovered for generating β-trimethylsilyl ketones cleanly involves the use of pyridinium chlorochromate. These end products may additionally be utilized as regiospecific enolate precursors,[35] thereby expanding the scope of this chemistry to include alkylative 1,2-keto transposition if desired.

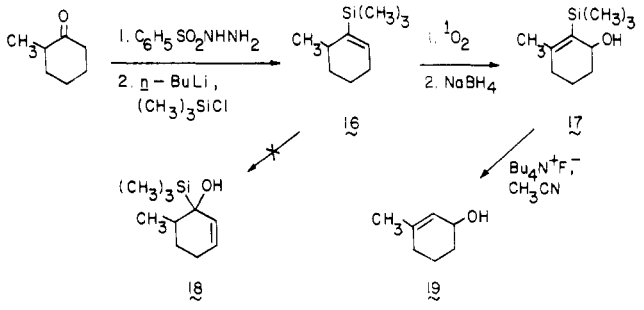
It should be noted that epoxidation of the vinylsilanes derived from α-tetralone and its 6-methoxy derivative under the standard conditions led directly to the β-tetralones (Table I). The precise course of these one-step transformations has not been elucidated. No epoxide intermediates were observed. Furthermore, 1,2-dihydronaphthalene (**16**) under identical conditions led cleanly to **17** in high yield. Thus, the presence of the 1-trimethylsilyl group is of paramount importance.

16 17

The present approach to 1,2-carbonyl transposition nicely complements the existing methods. It employs a different substrate, a vinylsilane, as the relay intermediate. Since these compounds are readily available from ketones[1] and their subsequent chemical manipulation is exceptionally efficient, the scheme comprises a promising technique for effecting the 1,2-migration of a carbonyl group. A major advantage of the sequence is found in the fact that no purification steps need be performed until final isolation of the transposed ketone. The nonrectified vinylsilane, epoxide, and alcohol are all directly suitable as is for the subsequent step; even residual solvent is fully compatible with the ensuing reagent.

Vinylsilane Photooxygenation. In view of the extensive control of regiochemistry which can be achieved by positioning a trimethylsilyl group on a carbon–carbon double bond or an oxiranyl ring, we anticipated that the silicon substituent might also direct the ene reaction of

Scheme II



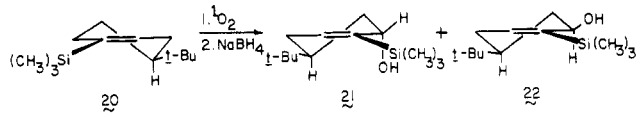
16 17 18 19

singlet oxygen with vinylsilanes for utilitarian synthetic purposes. The photooxygenation of olefins is recognized to be a reaction which is quite sensitive to electronic and steric effects.[36] Geometric requirements are high, and the molecular framework must allow the allylic hydrogen to be abstracted to attain coplanarity with the adjacent π orbital.[36]

It is presently recognized that the relative reactivities of sterically similar π systems toward singlet oxygen are controlled to a large extent by their ionization potentials.[37] Unsaturated systems of very high ionization potential are found to be unreactive to singlet oxygen. Because silicon (1.9) is more electropositive than carbon (2.55), the trimethylsilyl group should donate electrons to the vinyl moiety by an inductive mechanism. However, silicon also has empty low-lying d orbitals which can result in electron withdrawal by resonance with the π system. This interaction could deplete the π bond of electron density, lower the HOMO energy, and curtail reactivity. However, photoelectron spectroscopic data reveal that vinylsilanes actually have π HOMO energies rather comparable to those of structurally related all-carbon compounds. As an example, CH_2=$CHSiMe_3$ (−9.8 eV) has only a very slightly higher (more negative) ionization potential than CH_2=$CHCMe_3$ (−9.6 eV).[38] Thus these two effects, along with possible d_π–p_π hyperconjugative back-bonding, stabilize the HOMO to an extent which appears to be almost mutually compensatory. Accordingly, ene reactions were not expected to be electronically impeded if ionization potentials do serve as useful guides to reactivity.

The synthetic procedure herein utilized involved the customary dye-sensitization technique. The resulting allylic hydroperoxides were immediately reduced with sodium borohydride in methanol solution to the allylic alcohol (Scheme II). No attempt was made to analyze products at the hydroperoxide stage. A compilation of results may be found in Table IV.

Significantly, a single silylated allylic alcohol was isolated in each case. While two possible products could be expected to result from oxygenation α or β to the trimethylsilyl substituent, only the α-silylated allylic alcohol was detected. For conformational reasons, vinylsilanes such as **20** have quasi-axially locked hydrogens cis and



20 21 22

(31) For an excellent review of Si–X bond cleavages, consult: Boe, B. *J. Organomet. Chem.* **1976**, *107*, 139.

(32) For early reports concerning desilylation of β-silyl ketones in acidic media, see: (a) Whitmore, F. C.; Sommer, L. H.; Gold, J.; Van Strien, R. E. *J. Am. Chem. Soc.* **1947**, *69*, 1551; (b) Hauser, C. R.; Hance, C. R. *Ibid.* **1952**, *74*, 5091.

(33) For reports concerning Si–C cleavage by base, see: (a) Eaborn, C.; Jones, J. R.; Seconi, G. *J. Organomet. Chem.* **1976**, *116*, 83 and references cited therein; (b) Stork, G.; Ganem, B. *J. Am. Chem. Soc.* **1973**, *95*, 6152.

(34) (a) Brown, H. C.; Garg, C. P. *J. Am. Chem. Soc.* **1961**, *83*, 2952. (b) Brown, H. C.; Garg, C. P.; Liu, K.-T. *J. Org. Chem.* **1971**, *36*, 387.

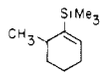
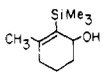
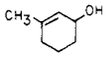
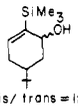
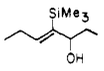
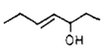
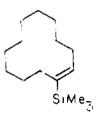
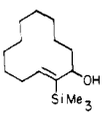
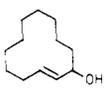
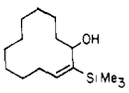
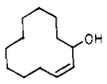
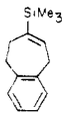
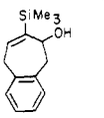
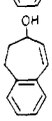
(35) (a) Nakamura, E.; Shimizu, M.; Kuwajima, I. *Tetrahedron Lett.* **1976**, 1699. (b) Nakamura, E.; Murafushi, T.; Shimizu, M.; Kuwajima, I. *J. Am. Chem. Soc.* **1976**, *98*, 2346.

(36) For general reviews, see: (a) Gollnick, K. *Adv. Photochem.* **1968**, *6*, 1. (b) Foote, C. S. *Acc. Chem. Res.* **1968**, *1*, 104; (c) Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395; (d) Denney, R. W.; Nickon, A. *Org. React.* **1973**, *20*, 133; (e) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359.

(37) Paquette, L. A.; Liotta, D. C.; Baker, A. D. *Tetrahedron Lett.* **1976**, 2681.

(38) (a) Mollère, P.; Bock, H.; Becker, G.; Fritz, G. *J. Organomet. Chem.* **1972**, *46*, 89. (b) Weidner, U.; Schweig, G. *Ibid.* **1972**, *39*, 261. (c) Bock, H.; Seidl, H. *Ibid.* **1968**, *13*, 87.

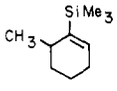
Table IV. 1,2-Oxidative Transposition of Vinylsilanes[a]

vinylsilane	α-silylated allylic alcohol	reaction time, h	conversion, %	isolated yield, %[b]	allylic alcohol	isolated yield, %
		12	12	25		51
		26	100	56		97
	 (cis/trans = 1:3)	30	50	59		96
		4	86	25		98
		–	–	16		100
		48	59	38		96
		–	–	9		96
		12	62	76		60[c]
		–	–	24		

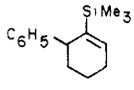
[a] All compounds were characterized by IR, NMR, and accurate mass spectral measurements. [b] These yields have been normalized to account for recovered starting material. [c] Partial dehydration occurs upon purification to give 30% benzocycloheptatriene.

trans to the *tert*-butyl group. Upon oxygenation, axial alcohol **21** proved to be the favored product in conformance with the "regioallowed" pathway.[22] The distinction between **21** and **22** rests on the following evidence. The product obtained upon column chromatography appeared to be homogeneous by ^{1}H NMR analysis of the *tert*-butyl and trimethylsilyl signals at 90 MHz. Notwithstanding, treatment of the sample with a lanthanide shift reagent such as Eu(fod)$_3$ caused the original pair of signals to separate nicely into twin sets, each in a ratio of 1:3. The *tert*-butyl group of the major isomer exhibited the greater $\Delta\delta$ and was assigned as **21** for reasons of spatial proximity. The trimethylsilyl singlet with the greater $\Delta\delta$ belongs to the minor isomer as expected for **22**. Additionally, the olefinic signal of the mixture consists of two merging mutliplets, the higher field component belonging to the minor alcohol. Ultimately, the structural assignment to the major component was confirmed by conversion with fluoride ion to *trans*-5-*tert*-butylcyclohexen-3-ol.[39] The 3:1 ratio of **21** to **22** obtained from **20** is identical with the ratio of axial/equatorial allylic alcohols produced upon photooxygenation of 4-*tert*-butylcyclohexene.[40]

Examples **23** and **24** more precisely define the requirement of axial hydrogen abstraction. Vinylsilane **23** un-

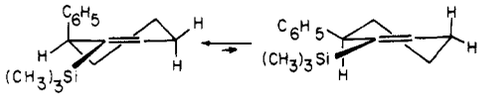


23



24

derwent slow photooxygenation during 12 h (12% conversion). The phenyl-substituted analogue was inert during the same elapsed time. This lack of reactivity can be rationalized in terms of allylic strain theory.[41] The bulky phenyl and trimethylsilyl groups are prevented from both residing in equatorial positions. Conformation **25a**

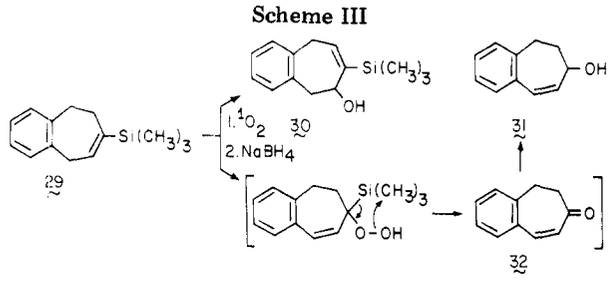


25a **25b**

with the phenyl substituent axially oriented is presumed to be dominant. In this conformation, the allylic hydrogen to be abstracted finds itself in an equatorial orientation and is therefore unavailable for the normal ene process. Importantly, an axial hydrogen is always available on the

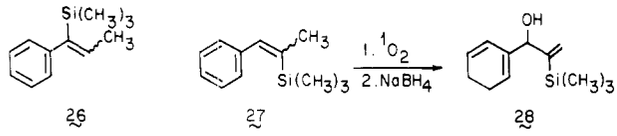
(39) Chamberlain, P.; Roberts, M. L.; Whitham, G. H. *J. Chem. Soc. B* **1970**, 1374.
(40) Jefford, C. W.; Boschung, A. F. *Helv. Chim. Acta* **1974**, *57*, 2242.
(41) Johnson, F. *Chem. Rev.* **1968**, *68*, 375.

Scheme III



opposite side of the double bond. However, this regioreversed hydrogen abstraction pathway is not followed, presumably for electronic reasons.[22] In **23**, the smaller size of the methyl group seemingly allows some degree of population of the conformation related to **25b**, and the oxidation proceeds slowly.

The powerful control which the trimethylsilyl group exerts on the regiochemistry of the ene reaction is nicely illustrated by the two similar vinylsilanes **26** and **27**.



Under conditions which transformed **27** to **28** (54% conversion), vinylsilane **26** was recovered in high yield. Again, no regioreversed reactivity (i.e., oxygenation α to silicon) was noted.

As a further test, the vinylsilane **29** was selected. Benzylic hydrogens are well-known to be abstracted in preference to unactivated hydrogens in other systems.[36] In the case of **29**, benzylic abstraction would lead to the regioreversed product **31** while regioallowed[22] abstraction of an unactivated hydrogen would give **30** (Scheme III). When the photooxygenation was performed, **30** predominated by a factor of 3:1. The lower pathway of the scheme shows the reactive intermediates presumed to be involved in the production of **31**. This mechanism was corroborated by changing the reducing agent (i.e., sodium borohydride) to aqueous sodium sulfite. Now the α,β-unsaturated ketone **32** was isolated in place of **31**. As a control experiment, olefin **33** was photooxygenated, and as anticipated, clean conversion exclusively to **34** was observed.

Further, we have determined that photooxygenation of acyclic or larger ring vinylsilanes affords mixtures of *Z* and *E* α-silylated allylic alcohols (Table IV) which can be efficiently separated by vapor-phase or column chromatography techniques.[42] The structures of the individual isomers were easily delineated on the basis of chemical shifts of the olefinic protons. In the cis isomers, the hydroxyl group shields the spatially proximate olefinic hydrogen; the same effects do not operate in the trans series. In the (*E*)- and (*Z*)-4-(trimethylsilyl)hept-4-en-3-ols, for example, the magnitude of $\Delta\delta$ was 0.45 ppm. For the cyclododecene isomers, the chemical shift difference was still larger (0.56 ppm).[43]

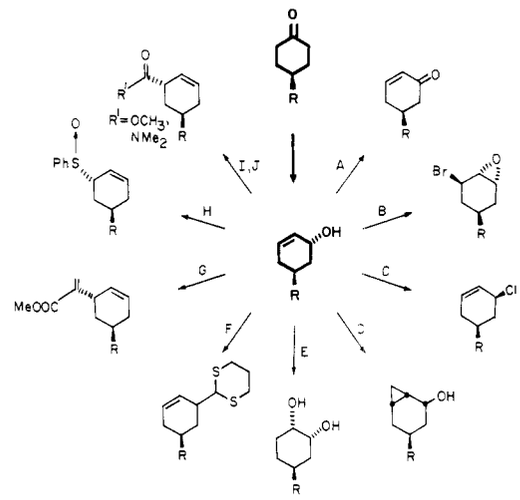
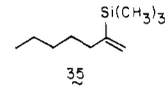


Figure 1. Some elaboration products of a transposed allylic alcohol. References to the reagents used are given in footnote 46.

A single type of vinylsilane has been observed not to undergo "regioallowed" photooxygenation when sterically permitted, viz., terminal systems such as **35**. Apparently a monosubstituted vinylsilane is too electron deficient to react at an appreciable rate.



The predescribed photooxygenation process allows for the conversion of a saturated ketone to a 1,2-transposed allylic alcohol. The final step (Scheme II), cleavage of the silicon–vinyl carbon bond, was accomplished by taking advantage of the affinity of fluoride ion for silicon and the accelerating effect of a β-hydroxyl group.[44] Chan had previously noted that silicon–vinyl carbon bonds are difficult or impossible to cleave under ordinary circumstances but that desilylation with fluoride ion proceeded with much greater facility when a β-hydroxyl substituent was present. This acceleration was explained in terms of hydrogen bonding of F^- to the hydroxyl group, thus positioning the nucleophile for attack on silicon. Presently, the most effective conditions uncovered for achieving such transformations involved heating with tetra-*n*-butylammonium fluoride (10 equiv) in dry acetonitrile. Requisite reaction times varied from 1 to 36 h, with the more flexible acyclic systems reacting faster. Of particular note here is the preservation of geometry about the π linkage during Si–C bond fission (Table IV).[45]

The versatility of this transposition method is illustrated by the examples provided in Table IV. In practical terms, its utilitarian nature does not stop here since the allylic alcohols so produced can in principle be converted by existing methodology into a wide range of functionalized molecules, some of which are illustrated in Figure 1.

(42) Gas-phase chromatographic separations should be restricted to the lower molecular weight systems where excessive temperatures are not required. At more elevated temperatures, conversion to allenes has been observed. See: Chan, T. H., et al. *Tetrahedron Lett.* **1974**, 171.

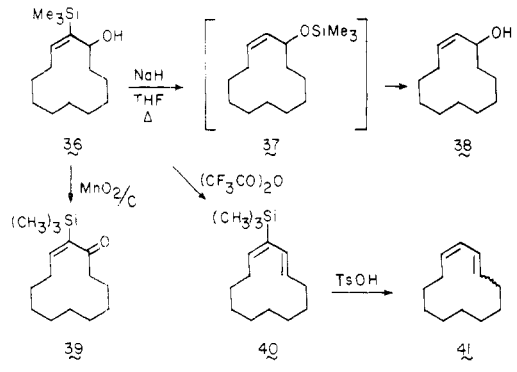
(43) Compare: (a) Martin, G. J.; Naulet, N.; Lefevre, F.; Martin, M. L. *Org. Magn. Reson.* **1972**, *4*, 121; (b) Sucrow, W.; Richter, W. *Chem. Ber.* **1971**, *104*, 3679.

(44) Chan, T. H.; Mychajlowskij, W. *Tetrahedron Lett.* **1974**, 3479.

(45) Compare: Snider, B. B.; Karras, M.; Conn, R. S. E. *J. Am. Chem. Soc.* **1978**, *100*, 4625.

(46) (a) Jefford, C. W.; Boschung, A. F. *Helv. Chim. Acta* **1974**, *57*, 2257. (b) Jefford, C. W.; Boschung, A. F. *Ibid.* **1977**, *60*, 2673. (c) Jefford, C. W.; Rimbault, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 295. (d) Higgins, R.; Foote, C. S.; Cheng, H. *Adv. Chem. Ser.* **1968**, *No. 77*, 102. (e) Foote, C. S.; Fujimoto, T. T.; Chang, Y. C. *Tetrahedron Lett.* **1972**, 45. (f) Stephenson, L. M.; McClure, D. E.; Sysak, P. K. *J. Am. Chem. Soc.* **1973**, *95*, 7888. (g) Hasty, N. M.; Kearns, D. R. *Ibid.* **1973**, *95*, 3380. (h) Nickon, A.; Chuang, V. I.; Daniels, P. J. L.; Denny, R. W.; DiGiorgio, J. B.; Isunetsugu, J.; Vilhuber, H. G.; Werstiuk, E. *Ibid.* **1972**, *94*, 5517. (i) Ashford, R. D.; Ogryzlo, E. A. *Ibid.* **1975**, *97*, 3604. (j) Kopecky, K. R.; van de Sande, J. H. *Can. J. Chem.* **1972**, *50*, 4034.

Scheme IV



Saturated β-trimethylsilyl alcohols are known to undergo syn elimination under basic conditions.[47] However, Chan has noted that such eliminations do not occur when the silicon atom is bonded to a trigonal center.[48] In fact, treatment of a silyl alcohol such as **36** (see Scheme IV) under their conditions led to no reaction. However, when **36** was treated with sodium hydride in refluxing tetrahydrofuran followed by an aqueous workup, the desilylated alcohol **38** was produced. Although we have not sought to determine the mechanism of this reaction, ^{1}H NMR evidence for the intervention of **37** has been obtained (Scheme IV). In the presence of activated manganese dioxide on charcoal,[49] **36** underwent slow oxidation (12 days) to give **39** (90%). When **36** was treated with 1 equiv of *p*-toluenesulfonic acid, dehydration was accompanied by desilylation to give cyclodeca-1,3-diene (**41**) in quantitative yield. Büchi and Wüest have reported that *p*-toluenesulfinic acid can be used to convert vinylsilanes to olefins.[50] While the conversion to a diene may not be useful, arresting the elimination at **40** would afford an unsymmetrically substituted diene system. This more selective dehydration could be effected with trifluoroacetic anhydride in pyridine; silyl diene **40** was isolated in 80% yield based on unrecovered starting material.

While this brief investigation of β-silyl alcohol chemistry is hardly exhaustive, it does suffice to indicate selected transformations which are possible. The significant aspects of vinylsilane photooxygenation are its regiospecificity and the ease with which the control center, the trimethylsilyl group, can be easily attached and subsequently removed if desired.

Experimental Section

Proton magnetic resonance spectra were recorded with Varian A-60A, EM-360, and T-60 spectrometers as well as a Bruker HX-90 spectrometer. Apparent splittings are given in all cases. Infrared spectra were recorded on a Perkin-Elmer Model 467 instrument. Mass spectra were determined on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

6-(Trimethylsilyl)spiro[4.5]dec-6-ene.[51] A 7.66-g (25 mmol) sample of spiro[4.5]decan-6-one benzenesulfonylhydrazone (mp 151–152.0 °C) was gradually added under nitrogen to a cold (−45 °C) solution containing 5 equiv (78.1 mL of a 1.6 M solution in hexane) of *n*-butyllithium in anhydrous TMEDA (200 mL). The resulting red solution was stirred at −45 °C for 15 min and at 0 °C for 4 h, at which point 4 equiv of freshly distilled chlorotrimethylsilane was added. After 4 h, water (100 mL) was introduced, and the mixture was extracted with pentane (300 mL). Following the customary workup[1] and chromatography on neutral alumina, there was obtained 3.48 g (66.7%) of the vinylsilane: ^{1}H NMR ($CDCl_3$) δ 6.97 (m, 1 H), 2.28–1.92 (m, 2 H), 1.79–1.32 (m, 12 H), 0.19 (s, 9 H); mass spectrum, *m/e* calcd 208.1647, obsd 208.1645. Anal. Calcd for $C_{13}H_{24}Si$: C, 74.92; H, 11.61. Found: C, 75.20; H, 11.62.

3-(Trimethylsilyl)cholestan-2-ene. This vinylsilane was prepared in the usual manner in 50% yield. However, the substance proved to be contaminated with a small amount of 2-cholestene which could not be completely removed by either high-pressure liquid chromatography or recrystallization. A sample was recrystallized from hexane and again from methanol: mp 158–165 °C; ^{1}H NMR ($CDCl_3$) δ 6.0–5.5 (m, 1 H), 2.1–0.7 (series of m, 46 H), 0.1 (s, 9 H); mass spectrum, *m/e* calcd 442.3995, obsd 442.4004.

(*E*)-4-(Trimethylsilyl)-3,4-epoxyheptane. (*E*)-4-(Trimethylsilyl)hept-3-ene (4.02 g, 23.7 mmol) was dissolved in dry dichloromethane (150 mL) buffered with sodium bicarbonate (4 g). The slurry was cooled to 0 °C, and *m*-chloroperbenzoic acid (85%, 5.28 g, 26 mmol) was added slowly. After 90 min, the solvent was evaporated and replaced with ether. The solution was extracted with water (1 × 60 mL), saturated sodium sulfite (2 × 60 mL) and sodium bicarbonate solutions (2 × 60 mL), and brine before drying. The solvent was evaporated to yield the epoxide as a colorless oil: 4.29 g (98%); ^{1}H NMR ($CDCl_3$) δ 2.7 (t, J = 5 Hz, 1 H), 1.9–0.8 (m, 12 H), 0.10 (s, 9 H); ν_{max} (film) 2965, 2880, 1465, 1252, 840, 752 cm^{-1}; mass spectrum, *m/e* calcd 186.1440, obsd 186.1444.

1-(Trimethylsilyl)-2-methyl-7-oxa-*cis*-bicyclo[4.1.0]heptane. 2-(Trimethylsilyl)-3-methylcyclohexene (1.16 g, 6.91 mmol) was dissolved in dry dichloromethane (50 mL) buffered with sodium bicarbonate (1 g). To the ice-cooled, stirred solution was slowly added *m*-chloroperbenzoic acid (85%, 1.44 g, 7.1 mmol). After the addition was complete, the slurry was allowed to warm to room temperature and stirred for 12 h. The milky solution was extracted with saturated sodium sulfite (2 × 50 mL) and sodium bicarbonate solutions (2 × 50 mL) and brine prior to being dried. The solvent was removed to yield a colorless oil (1.13 g, 89%) consisting of 38% 1-(trimethylsilyl)-*syn*-2-methyl-7-oxa-*cis*-bicyclo[4.1.0]heptane (**5**) [^{1}H NMR ($CDCl_3$) δ 3.0 (**ABX** m, 1 H), 2.3–1.7 (m, 3 H), 1.6–1.0 (m, 5 H), 1.05 (d, J = 7 Hz, 3 H), 0.10 (s, 9 H)] and 62% 1-(trimethylsilyl)-*anti*-2-methyl-7-oxa-*cis*-bicyclo[4.1.0]heptane (**6**) [^{1}H NMR ($CDCl_3$) δ 2.9 (**ABX** m, 1 H), 2.3–1.7 (m, 3 H), 1.6–1.0 (m, 4 H), 1.05 (d, J = 7 Hz, 3 H), 0.10 (s, 9 H); mass spectrum, *m/e* calcd 184.1283, obsd 184.1287]. The two isomers were separated by VPC on a 4 ft × 0.25 in., 10% SF-96 column at 140 °C.

6,7-Epoxy-6-(trimethylsilyl)spiro[4.5]decane.[51] To a mixture of the vinylsilane (2.08 g, 10.0 mmol) and sodium carbonate (880 mg, 10.5 mmol) in dichloromethane (20 mL) was added 2.13 g (85%, 10.5 mmol) of *m*-chloroperbenzoic acid. The usual workup furnished 2.04 g (90.9%) of epoxysilane as a clear oil: ^{1}H NMR ($CDCl_3$) δ 2.87 (m, 1 H), 1.75–1.55 (m, 8 H), 1.48–1.25 (m, 6 H), 0.12 (s, 9 H); mass spectrum, *m/e* calcd 224.1596, obsd 224.1600.

1-(Trimethylsilyl)-2-isopropyl-5-methyl-7-oxa-*cis*-bicyclo[4.1.0]heptane. By use of the procedure described previously (90-min reaction time), this epoxysilane was produced in 77% yield as a clear oil: ^{1}H NMR ($CDCl_3$) δ 2.9 (br s, 1 H), 2.3–1.2 (m, 7 H), 1.1–0.8 (m, 9 H), 0.10 (s, 9 H); mass spectrum, *m/e* calcd 266.1753, obsd 226.1758.

1-(Trimethylsilyl)-4-*tert*-butyl-7-oxa-*cis*-bicyclo[4.1.0]heptane. Following the procedure developed previously (12-h reaction time), an epoxide mixture was obtained in 87% yield as a white solid: mp 49–52 °C; ^{1}H NMR ($CDCl_3$) δ 3.2–2.9 (**ABX** m, 1 H), 2.4–1.0 (m, 7 H), 0.9 (s, 9 H), 9.1 (s, 9 H). The two isomers proved inseparable by thin-layer or vapor-phase chromatography under a variety of conditions. However, reduction studies indicated the isomer ratio to be 60% anti and 40% syn.

4,5-Benzo-1-(trimethylsilyl)-8-oxa-*cis*-bicyclo[5.1.0]oct-4-ene. Following the epoxidation procedure described previously (90-min reaction time), the epoxysilane was obtained quantitatively as a clear oil: ^{1}H NMR ($CDCl_3$) δ 7.15 (s, 4 H), 3.4–3.2 (m, 2 H), 3.0–1.6 (m, 5 H), 0.05 (s, 9 H); ν_{max} (film) 3015, 2980, 1670, 1495, 1455, 1250, 1150, 1100, 840, 750 cm^{-1}; mass spectrum, *m/e* calcd 232.1283, obsd 232.1289.

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(48) Chan, T. H.; Mychajlowskij, W. *Tetrahedron Lett.* **1974**, 171.
(49) Carpino, L. *J. Org. Chem.* **1970**, *35*, 3971.
(50) Büchi, G.; Wüest, H. *Tetrahedron Lett.* **1977**, 4305.
(51) The authors are indebted to Mr. Rhys Daniels for conducting these experiments.

2β-(Trimethylsilyl)-2α,3α-epoxycholestane. The epoxidation was performed as usual during 90 min to give the epoxysilane in 90% yield: mp 183–188 °C (from acetone–ether); ^{1}H NMR ($CDCl_3$) δ 2.9 (d, J = 6 Hz, 1 H), 2.1–1.6 (m, 43 H), 0.1 (s, 9 H); mass spectrum, m/e calcd 458.3944, obsd 458.3952.

3-Methyl-*cis*-2-(trimethylsilyl)cyclohexanol. A solution of 1-(trimethylsilyl)-2-methyl-7-oxa-*cis*-bicyclo[4.1.0]heptane (**5/6** mixture; 1.45 g, 7.9 mmol) in dry ether (10 mL) was slowly added to a slurry of lithium aluminum hydride (0.34 g, 9.0 mmol) in dry ether (40 mL) and the solution was cooled to 0 °C under argon. The reaction mixture was stirred at 0 °C for 15 min and then allowed to warm to room temperature with continued stirring for 5 h. The mixture was cooled to 0 °C and quenched with a saturated solution of sodium sulfate. When the solids turned completely white, the mixture was suction filtered, the solids were washed with ether (2 × 20 mL), and the filtrate was dried. The solvent was evaporated, and the residue was distilled to give the silyl alcohol as a clear oil: bp 70 °C (0.5 torr); 1.22 g (83%); ^{1}H NMR ($CDCl_3$) δ 4.10 (br s, 1 H), 2.1–0.9 (m, 8 H), 0.95 (d, J = 6 Hz, 3 H), 0.16 (s, 9 H); ν_{max} (film) 3480, 2940, 2880, 1460, 1250, 1030, 940, 830, 745, 685 cm^{-1}.

4-(Trimethylsilyl)-3-heptanol. Following the reduction procedure developed previously, the corresponding epoxide afforded the alcohol in 52% distilled yield: bp 58 °C (0.5 torr); ^{1}H NMR ($CDCl_3$) δ 4.6 (s, 1 H), 3.8–3.4 (m, 1 H), 2.0–0.8 (m, 12 H), 1.10 (s, 9 H); ν_{max} (film) 3400, 2950, 2870, 1450, 1250, 1100, 1060, 1020, 960, 840, 750 cm^{-1}.

1-Isopropyl-2-(trimethylsilyl)-4-methylcyclohexan-3-ol. A three-necked flask equipped with a condenser, a nitrogen inlet, and an addition funnel was charged with dry tetrahydrofuran (40 mL) and lithium aluminum hydride (0.15 g, 4.0 mmol). To the stirred slurry was added a solution of the epoxysilane (0.85 g, 3.8 mmol) in dry tetrahydrofuran (10 mL). The mixture was refluxed for 40 h, cooled to 0 °C, and quenched with a saturated solution of sodium sulfate. The while solids were filtered and triturated with boiling ether (2 × 50 mL). The combined filtrates were dried and evaporated to yield the silyl alcohol: 0.51 g (61%); ^{1}H NMR ($CDCl_3$) δ 3.72 (m, 1 H), 2.1–1.1 (m, 8 H), 1.1–0.7 (m, 9 H), 0.10 (s, 9 H). An M^+ peak was not seen, and the base peak at m/e 138 corresponds to loss of trimethylsilanol.

***cis*-6-(Trimethylsilyl)spiro[4.5]decan-7-ol.**[51] From 1.75 g (7.8 mmol) of the epoxysilane and 300 mg (7.9 mmol) of lithium aluminum hydride in 125 mL of ether (24 h, 25 °C), there was isolated 1.68 g (95.1%) of the silyl alcohol: ^{1}H NMR ($CDCl_3$) δ 4.0 (m, 1 H), 1.65–1.37 (m, 14 H), 0.94 (m, 1 H), 0.29 (s, 9 H).

Lithium Aluminum Hydride Reduction of 1-(Trimethylsilyl)-4-*tert*-butyl-7-oxa-*cis*-bicyclo[4.1.0]heptane (7/8 Mixture). Following the procedure given previously for the **5/6** mixture, the reaction mixture was subjected to careful gas-phase chromatography (5 ft × 0.25 in. column, Carbowax 20-M, 165 °C). Three compounds were identified with the following retention times and NMR data: (a) retention time 4.5 min, starting epoxide (33%); (b) retention time 7.5 min, 1-trimethyl-*cis*- and -*trans*-4-*tert*-butylcyclohexanols (**9/10**, 51%), ^{1}H NMR ($CDCl_3$) δ 1.9–0.8 (m, 10 H), 0.85 (s, 9 H), 0.03 (s, 9 H); (c) retention time 11.5 min, *cis*-1-(trimethylsilyl)-*trans*-4-*tert*-butylcyclohexan-2-ol (**11**, 16%), ^{1}H NMR ($CDCl_3$) δ 4.2–4.1 (m, 1 H), 2.0–0.8 (m, 8 H), 0.80 (s, 9 H), 0.00 (s, 9 H).

1,2-Benzo-*cis*-5-(trimethylsilyl)cyclohepten-4-ol. A three-necked flask equipped with a condenser, a nitrogen inlet, and an addition funnel was charged with dry ether (80 mL) and lithium aluminum hydride (0.17 g, 4.4 mmol). To the stirred slurry was added the epoxysilane (1.01 g, 4.26 mmol) in dry ether (20 mL). The mixture was refluxed for 27 h before being cooled to 0 °C and quenched with a saturated solution of sodium sulfate. The white mixture was filtered, with the salts being leached twice with boiling ether. The combined filtrates were dried and evaporated to yield the silyl alcohol in quantitative yield: ^{1}H NMR ($CDCl_3$) δ 7.15 (s, 4 H), 4.4–4.2 (m, 1 H), 3.2–2.7 (m, 4 H), 2.1–1.1 (m, 4 H), 0.06 (s, 9 H); ν_{max} (film) 3440, 2960, 1500, 1455, 1250, 1030, 840, 750 cm^{-1}. No M^+ peak was seen; m/e 144 (80% of base peak) corresponds to loss of trimethylsilanol, while m/e 120 (base peak) corresponds to loss of benzocyclobutene.

Lithium Aluminum Hydride/Aluminum Chloride Reduction of 7/8. A three-necked flask equipped with an overhead stirrer, an addition funnel, and a nitrogen inlet was charged with dry ether and lithium aluminum hydride. The slurry was cooled to 0 °C before the addition of anhydrous aluminum chloride. The ratio of lithium aluminum hydride to aluminum chloride was varied (Table III). The mixture was stirred in the cold (0 °C) for 5 min and at room temperature for 15 min and was recooled to 0 °C. A solution of the epoxysilane in dry ether was added dropwise. Once the addition was complete, the solution was stirred at 0 °C for an additional 30 min before being allowed to warm to room temperature for an additional 1–3 h. The excess reducing agent was destroyed by the addition of a saturated solution of sodium sulfate until the solids turned white. The solids were filtered and extracted twice with boiling ether, and the combined filtrates were dried and evaporated. Separation of the products (1 ft × 0.25 in. column, 10% SE-30, 155 °C) yielded the product distributions indicated in Table III. For **12**: ^{1}H NMR ($CDCl_3$) δ 4.1–3.7 (m, 1 H), 2.1–0.4 (m, 9 H), 0.80 (s, 9 H), 0.03 (s, 9 H).

3α-(Trimethylsilyl)cholestan-2α-ol and 3β-(Trimethylsilyl)cholestan-3α-ol. The reduction was performed as previously described except for the reflux time which was extended to 48 h. The crude alcohol mixture was obtained in quantitative yield in approximately a 1/4 ratio (2α-ol/3α-ol): ^{1}H NMR ($CDCl_3$) δ 3.8–3.6 (m, 0.20 H), 2.1–0.6 (m, 44 H), 0.12 and 0.03 (s, 9 H); mass spectrum, m/e calcd 460.4100, obsd 460.4109. No attempt was made to separate the silyl alcohols; the mixture was directly oxidized.

Lithium Aluminum Deuteride/Aluminum Chloride Reduction of 7/8. The reduction was performed as previously described by using lithium aluminum deuteride in place of the protio analogue. The crude oil obtained was separated into its constituents by gas-phase chromatography (6 ft × 0.25 in. column, 5% Carbowax 20-M, 134 °C) as follows. (a) The compounds with retention times of 14 and 15 min (6 and 4%) were assigned as the cis and trans isomers of 1-(trimethylsilyl)-2-deuterio-4-*tert*-butylcyclohexanol: ^{1}H NMR ($CDCl_3$) δ 1.9–0.9 (m, 9 H), 0.74 (s, 9 H), 0.00 and 0.10 (s, 9 H); mass spectrum, m/e calcd 229.1972, obsd 229.1978. (b) The compound with a retention time of 17 min (69%) was assigned as **13**: ^{1}H NMR ($CDCl_3$) δ 4.2–4.0 (m, 1 H), 1.9–0.9 (m, 8 H), 0.71 (s, 9 H), –0.10 (s, 9 H); mass spectrum, m/e calcd 229.1972, obsd 229.1978 (weak), m/e calcd 139.1471, obsd 139.1474 (loss of trimethylsilanol). (c) The compound with a retention time of 26 min (21%) was assigned as **14**: ^{1}H NMR ($CDCl_3$) δ 4.0–3.6 (m, 1 H), 1.9–0.8 (m, 8 H), 0.64 (s, 9 H), –0.10 (s, 9 H); mass spectrum, m/e calcd 139.1471, obsd 139.1474 (loss of trimethylsilanol, no parent ion seen).

4-*tert*-Butylcyclohexene-*1-d* (15). A sample of **13** (18.3 mg, 0.80 mmol) was dissolved in a slurry of dry tetrahydrofuran (5 mL) and sodium hydride (50% in oil, 8 mg, 0.17 mmol) which had been washed free of oil with pentane. The reaction mixture was refluxed for 15 h, excess hydride was decomposed with 2 drops of water, and the solution was dried. The sole product isolated by gas-phase chromatography (1 ft × 0.25 in. column, SE-30, 90 °C) with a retention time of 3 min was the deuterated olefin: 2.7 mg (25%); ^{1}H NMR ($CDCl_3$) δ 5.7–5.5 (br s, 1 H), 2.1–1.0 (m, 7 H), 0.74 (s, 9 H); mass spectrum, m/e 139.1471, obsd 139.1474.

Spiro[4.5]decan-7-one.[51] To a stirred solution of the silyl alcohol (500 mg, 2.2 mmol) in ether (5 mL) was added a solution of sodium dichromate dihydrate (220 mg, 0.74 mmol) and 2.21 g (22 mmol) of concentrated sulfuric acid diluted to 5 mL with water. After 3 h, the ether layer was separated and the aqueous layer was extracted with ether (10 mL). The combined organic layers were washed with a few milliliters of 5% sodium bicarbonate solution and a few milliliters of brine, dried, and evaporated. There remained 222 mg (66%) of transposed ketone: ^{1}H NMR ($CDCl_3$) δ 2.14 (m, 4 H), 1.81–1.14 (series of m, 12 H); mass spectrum, m/e calcd 152.1201, obsd 152.1203. The semicarbazone had a melting point of 211–211.5 °C (lit.[8] mp 215–217 °C).

Brown Oxidation of 5-*tert*-Butyl-2-(trimethylsilyl)-cyclohexanol. Unpurified silyl alcohol mixture **11/12** (1.96 g, 8.6 mmol) was dissolved in ether (3 mL), and to this ice-cold stirred solution was added dropwise a solution of sodium dichromate (0.86 g, 2.87 mmol) in water (2 mL) and concentrated sulfuric acid (2.37 g, 23.0 mmol). Upon completion of the addition, the two-phase mixture was stirred vigorously at room temperature for 2 h and diluted with ether. The organic layer was separated, and the aqueous phase was extracted with ether (2 × 3 mL). The combined organic layers were extracted with a saturated solution of

sodium bicarbonate (2 × 3 mL) and brine prior to drying. Upon evaporation of the solvent, the remaining oil was determined to be 3-*tert*-butylcyclohexanone (1.25 g, 83%).[52]

Brown Oxidation of 4-(Trimethylsilyl)-3-heptanol. Following the procedure described above, a 64% distilled (bp 45 °C, 30 torr) yield of 3-heptanone[53] was obtained: ^{1}H NMR ($CDCl_3$) δ 2.4 (overlapping m, 4 H), 2.0–1.0 (m, 10 H).

Brown Oxidation of 2-(Trimethylsilyl)-3-methylcyclohexanol. Following the procedure described above, an 84% yield of 3-methylcyclohexanone[54] was realized: ^{1}H NMR ($CDCl_3$) δ 2.4–1.0 (m, 9 H), 1.0 (d, J = 5 Hz, 3 H); ν_{max} (film) 2940, 1725, 1260, 1230, 1061, 845 cm^{-1}.

Carvomenthone. Following the procedure described above, the title ketone was obtained in 90% yield: ^{1}H NMR ($CDCl_3$) δ 2.5–2.1 (m, 3 H), 1.9–1.2 (m, 6 H), 1.1 (d, J = 7 Hz, 3 H), 0.9 (d, J = 6 Hz, 6 H); mass spectrum, m/e calcd 154.1358, obsd 154.1362.

1,2-Benzocyclohepten-4-one. Following the same procedure, the ketone was obtained as a viscous oil in 63% yield:[55] 2,4-dinitrophenylhydrazone, mp 169.5–170 °C (lit.[56] mp 169–170 °C); ^{1}H NMR ($CDCl_3$) δ 7.16 (s, 4 H), 3.7 (s, 2 H), 3.1–2.8 (pseudo t, 2 H), 2.7–2.4 (pseudo t, 2 H), 2.2–1.6 (m, 2 H); mass spectrum, m/e calcd 160.0888, obsd 160.0891.

Cholestan-2- and -3-ones. The Brown oxidation was carried out as previously described, and the crude product was recrystallized from methanol/ether; mp 90–125 °C. The material could be partially separated by high-pressure liquid chromatography with cholestan-2-one eluting (hexane/ether, 10/1) first in 9% yield (mp 122–126 °C) followed by a mixture of the two cholestanones (mp 94–100 °C) and finally cholestan-3-one (mp 126–128 °C) in 41% yield.[57] The fractions containing cholestan-3-one were verified by a mixture melting point determination with an authentic sample; no depression was seen. The ^{1}H NMR spectra of the two cholestanones were also slightly different, with the last fraction again comparing identically with the cholestan-3-one spectrum: ^{1}H NMR ($CDCl_3$) δ 2.5–2.0 (m, 4 H), 2.1–0.6 (m, 42 H). The cholestan-2-one spectrum has minor differences: ^{1}H NMR ($CDCl_3$) δ 2.15 (m, 4 H) 2.1–0.6 (m, 42 H); mass spectrum, m/e calcd 386.3548, obsd 386.3554.

Pyridinium Chlorochromate Oxidation[58] of 2-(Trimethylsilyl)-3-methylcyclohexanol. Pyridinium chlorochromate (2.15 g, 10 mmol) was slurried in dry dichloromethane (50 mL), and the unpurified silyl alcohol (6.5 mmol) was added. The slurry turned black very rapidly, and the progress of reaction was monitored by thin-layer chromatography [silica gel eluted with pentane/methylene chloride (5/1)]. The reaction was allowed to continue for 2 h whereupon it was diluted with 4 volumes of ether. The liquid was filtered through a short column of Florisil to remove inorganic material. The chromium salts were washed with additional ether, and the combined filtrates were evaporated and distilled (bp 40–50 °C, 0.3 torr) to yield 2-(trimethylsilyl)-3-methylcyclohexanone: 0.62 g (51%); bp 55–60 °C (0.5 torr); ^{1}H NMR ($CDCl_3$) δ 2.4–1.0 (m, 9 H), 1.1 (d, J = 5 Hz, 3 H), 0.10 (s, 9 H); ν_{max} (film) 2960, 1715, 1255, 840 cm^{-1}.

β-Tetralone. 1-(Trimethylsilyl)-3,4-dihydronaphthalene (0.38 g, 1.9 mmol) dissolved in dry dichloromethane (25 mL) with sodium bicarbonate added as a buffer was cooled to 0 °C. To this slurry was added *m*-chloroperbenzoic acid (85%, 0.49 g, 2.4 mmol). The reaction mixture was stirred in the cold (0 °C) for 2 h under argon to prevent air oxidation of the product to β-naphthol. The solvent was evaporated and replaced with ether. The solution was washed with water (1 × 20 mL), a saturated solution of sodium sulfite (2 × 20 mL), a saturated solution of sodium bicarbonate (2 × 20 mL), and brine prior to being dried. After evaporation of solvent, the residue proved to be β-tetralone, the ^{1}H NMR spectrum of which was identical with that of an authentic sample: 0.21 g (83%); ^{1}H NMR ($CDCl_3$) δ 7.1 (s, 4 H), 3.55 (s, 2 H), 3.1–2.8 (**ABXY**, pseudo t, 2 H), 2.6–2.3 (AB**XY**, pseudo t, 2 H).

4-Methoxy-β-tetralone. The oxidation, which was performed as described above, yielded the translocated ketone as a semisolid in 96% yield: ^{1}H NMR ($CDCl_3$) δ 7.2–6.6 (m, 3 H), 3.8 (s, 3 H), 3.5 (s, 2 H), 3.1–2.8 (**ABXY**, pseudo t, 2 H), 2.6–2.3 (AB**XY**, pseudo t, 2 H).

General Photooxygenation Procedure. The vinylsilane was dissolved in methanol (5 g/200 mL) along with rose bengal (1 mg/1 mL) as sensitizer. The solution was irradiated through an air- and water-cooled Pyrex well with a Sylvania DYV bulb while oxygen was bubbled continuously through a frit at the bottom of the well. The dye was replenished if necessary (because of bleaching) by adding a small amount of a concentrated solution about every 15 h.

The oxidized reaction mixture was poured into an Erlenmeyer flask and sodium borohydride (1 molar equiv) was slowly added. After being stirred for at least 1 h, the mixture was concentrated and dissolved in ether. The organic layer was extracted twice with water to remove most of the rose bengal. The last trace of dye was removed by adsorption onto basic alumina and passage through a 2-cm plug of basic alumina. The clear eluate was dried and evaporated to give a mixture of starting vinylsilane and the product which could be easily separated by chromatography (silica gel, elution with 50% ether/hexane).

Spectral Data for Photooxygenation Products. 3-Methyl-2-(trimethylsilyl)cyclohex-2-en-1-ol: mp 44–47.5 °C; ^{1}H NMR ($CDCl_3$) δ 4.3–4.1 (m, 1 H), 2.2–1.0 (m, 10 H), 0.1 (s, 9 H).

2-(Trimethylsilyl)cyclohex-2-enol: ^{1}H NMR ($CDCl_3$) δ 6.10 (br t, J = 3 Hz, 1 H), 4.24 (br s, 1 H), 2.2–1.6 (br m, 7 H), 0.17 (s, 9 H). Anal. Calcd for $C_9H_{18}OSi$: C, 63.47; H, 10.65. Found: C, 63.39; H, 10.64.

2-(Trimethylsilyl)-5-*tert*-butylcyclohex-2-en-1-ol: ^{1}H NMR ($CDCl_3$) δ 6.2–5.8 (m, 1 H), 4.45–4.2 (m, 1 H), 2.1–1.7 (m, 2 H), 1.6–1.1 (m, 4 H), 0.87 (s, 9 H), 0.03 (s, 9 H); mass spectrum, m/e calcd 226.1753, obsd 226.1758; syn/anti ratio of 1/3. Anal. Calcd for $C_{13}H_{28}OSi$: C, 68.96; H, 11.57. Found: C, 68.96; H, 11.44.

(*E*)-4-(Trimethylsilyl)hept-4-en-3-ol: ^{1}H NMR ($CDCl_3$) δ 5.64 (dt, J = 7, 1 Hz, 1 H), 4.48 (d t, J = 6, 1 Hz, 1 H), 2.6–1.8 (m, 2 H), 1.7–1.2 (m, 3 H), 1.1–0.7 (m, 6 H), 0.04 (s, 9 H). Anal. Calcd for $C_{10}H_{22}OSi$: C, 64.45; H, 11.90. Found: C, 64.23; H, 11.78.

(*Z*)-4-(Trimethylsilyl)hept-4-en-3-ol: ^{1}H NMR ($CDCl_3$) δ 6.17 (dt, J = 7, 1 Hz, 1 H), 3.99 (t, J = 6 Hz, 1 H), 2.6–1.8 (m, 2 H), 1.7–1.2 (m, 3 H), 1.1–0.7 (m, 6 H), 0.08 (s, 9 H); for the mixture of *E* and *Z* isomers, ν_{max} (film) 3400, 2960, 1620, 1460, 1250, 1000, 840, 755, 685 cm^{-1}; mass spectrum, m/e calcd 186.1440, obsd 186.1444.

(*Z*)-2-(Trimethylsilyl)cyclododec-2-en-1-ol: ^{1}H NMR ($CDCl_3$) δ 6.25 (t, J = 7 Hz, 1 H), 4.27 (br t, 1 H), 2.5–2.0 (m, 2 H), 1.9–1.1 (m, 17 H), 0.13 (s, 9 H).

(*E*)-2-(Trimethylsilyl)cyclododec-2-enol: ^{1}H NMR ($CDCl_3$) δ 5.70 (ddd, J = 11, 4.5, and 1 Hz, 1 H), 4.80 (br t, J = 5.5 Hz, 1 H), 2.8–2.1 (m, 2 H), 2.0–0.7 (m, 17 H), 0.07 (s, 9 H); for the mixture of *E* and *Z* isomers, ν_{max} (film) 3370, 2940, 2860, 1605, 1465, 1250, 1010, 840, 760 cm^{-1}.

Photooxygenation of 4,5-Benzo-1-(trimethylsilyl)cyclohepta-1,4-diene. Following the general procedure, two products are obtained as follows. **5,6-Benzo-2-(trimethylsilyl)cyclohepta-2,5-dien-1-ol:** ^{1}H NMR ($CDCl_3$) δ 7.2–6.7 (m, 4 H), 5.95 (br d, J = 6 Hz, 1 H), 3.4–3.0 (m, 2 H), 2.9–2.6 (m, 1 H), 2.6–2.2 (m, 2 H), 0.05 (s, 9 H); mass spectrum, m/e calcd 232.1283, obsd 232.1289. **4,5-Benzocyclohepta-2,4-dienol:** ^{1}H NMR ($CDCl_3$) δ 7.2–7.1 (br s, 4 H), 6.40 (dd, J = 12, 1 Hz), 5.90 (dd, J = 12, 1 Hz, 1 H), 4.6–4.2 (m, 1 H), 3.2–1.8 (br m, 5 H).

3-Phenyl-2-(trimethylsilyl)propen-3-ol: ^{1}H NMR ($CDCl_3$) δ 7.26 (s, 5 H), 5.90 (dd, J = 2.4, 1.6 Hz, 1 H), 5.51 (dd, J = 2.4, 1.4 Hz, 1 H), 5.15 (br t, J = 1.5 Hz, 1 H), 1.96 (s, 1 H), 0.08 (s, 9 H). Anal. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79. Found: C, 69.77; H, 8.80.

General Tetra-*n*-butylammonium Fluoride Desilylation Procedure. 5-*tert*-Butylcyclohex-2-enol. The silyl alcohol (100 mg, 0.442 mmol) was dissolved in dry acetonitrile (2 mL), and a solution of tetra-*n*-butylammonium fluoride in acetonitrile

(52) This product exhibited a ^{1}H NMR spectrum identical with that found in: "The Sadtler Standard Spectra"; 1972; no. 5740.

(53) This product was spectrally identical with that reported by: Pouchert, C. J.; Campbell, J. R. "The Aldrich Library of NMR Spectra"; 1974; Vol. 2, p 108B.

(54) Connolly, J. D.; McCrindle, R. *Chem. Ind. (London)* **1965**, 379.

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(56) (a) Crabb, T. A.; Schofield, K. *J. Chem. Soc.* **1958**, 4276. (b) Page, G. A.; Tarbell, D. S. *J. Am. Chem. Soc.* **1953**, *75*, 2053.

(57) Both cholestanones have reported melting points of 128 °C.

(58) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

(2 M, 2.2 mL, 4.4 mmol) was added.[59] The mixture was heated to reflux for 36 h, cooled, diluted with ether (10 mL), washed with water (2 × 10 mL) and brine, and dried. The evaporated residue was chromatographed (silica gel, elution with 50% ether/hexane) to yield the desilylated product as a clear liquid: 65 mg (96%); ^{1}H NMR ($CDCl_3$) δ 5.85–5.5 (m, 1 H), 4.3–3.8 (m, 1 H), 2.2–1.0 (br m, 6 H), 0.80 (s, 9 H).[39]

Reaction Time and Spectral Data for the Desilylated Allylic Alcohols. 3-Methylcyclohex-2-enol:[60] 1.5 h; ^{1}H NMR ($CDCl_3$) δ 5.7–5.3 (m, 1 H), 4.3–4.0 (m, 1 H), 2.1–1.4 (m, 7 H), 1.7 (br s, 3 H).

Cyclohex-2-enol:[61] 1 h; ^{1}H NMR ($CDCl_3$) δ 5.7 (br s, 2 H), 4.2–3.9 (m, 1 H), 2.1–1.1 (m, 7 H).

(*E*)-Hept-4-en-3-ol:[60] 1 h; ^{1}H NMR ($CDCl_3$) δ 5.8–5.1 (m, 2 H), 3.84 (br q, J = 6 Hz, 1 H), 2.2–0.6 (br m, 11 H).

(*Z*)-Hept-4-en-3-ol:[43a] 1 h; ^{1}H NMR ($CDCl_3$) δ 5.6–5.0 (m, 2 H), 4.24 (br q, J = 7 Hz, 1 H), 2.4–0.6 (br m, 11 H).

(*E*)-Cyclododec-2-enol: 21 h; ^{1}H NMR ($CDCl_3$) δ 5.6–5.1 (m, 2 H), 4.3–3.8 (m, 1 H), 2.5–0.6 (m, 19 H); mass spectrum, m/e calcd 182.1671, obsd 182.1674.

(*Z*)-Cyclododec-2-enol: 1 h; ^{1}H NMR ($CDCl_3$) δ 5.6–5.1 (m, 2 H), 4.9–4.4 (m, 1 H), 2.6–0.6 (m, 19 H).

5,6-Benzocyclohepta-1,5-dien-3-ol: 1.5 h; ^{1}H NMR ($CDCl_3$) δ 7.13 (s, 4 H), 6.47 (dt, J = 11, 2 Hz, 1 H), 5.78 (dt, J = 11, 5 Hz, 1 H), 4.4–4.0 (m, 1 H), 3.4–2.3 (m, 4 H), 2.0 (s, 1 H).

(*Z*)-Cyclododec-2-enol. A solution of wet tetraethylammonium fluoride (several-fold excess) in dry acetonitrile (15 mL) was heated so that any water could be azeotroped out of the reaction vessel. The volume removed by distillation was replaced with dry acetonitrile, and the silyl alcohol (50 mg, 0.20 mmol) was added. The solution was heated to reflux, and the progress of reaction was monitored by thin-layer chromatography (silica gel, elution with 50% ether/hexane) for 75 min. The solution was cooled and evaporated. The residue, taken up in ether, was extracted with water (2 × 10 mL) and brine and dried. The evaporated residue was pure product (27 mg, 76%) which was identical with that obtained above.

(*Z*)-Cyclododec-2-enol. Sodium hydride (50%, 30 mg, 0.4 mmol) in oil was placed in a dry flask, washed free of oil with pentane (3 × 5 mL), and covered with dry tetrahydrofuran (5 mL). To this slurry was added the silyl alcohol (50 mg, 0.20 mmol), and the mixture was heated at reflux for 21 h. The crude reaction mixture was carefully diluted with wet ether, washed with water, dried, and evaporated. The residue was purified by chromatography (neutral alumina, elution with ether, R_f 0.9) to yield the allylic alcohol as a clear liquid (16 mg, 45%). The ^{1}H NMR spectrum was identical with that previously obtained.

(*Z,E*)- and (*Z,Z*)-2-(Trimethylsilyl)cyclododeca-1,3-diene. A solution of dry pyridine (2 mL) and trifluoroacetic anhydride (52 mg, 0.20 mmol) was cooled to 0 °C. To this cold solution was added the silyl alcohol (50 mg, 0.20 mmol) before the solution was allowed to warm to room temperature for 13 h. By thin-layer chromatographic analysis (silica gel eluted with 10% ether/hexane), starting material was seen to remain. Therefore, the reaction mixture was heated to 70 °C for 5 min. The solution was cooled, diluted with pentane, washed with water (3 × 5 mL), and dried. The residue upon evaporation of solvent was chromatographed (silica gel, elution with 10% ether/hexane). There was obtained 26 mg (56%) of the silylated diene: ^{1}H NMR ($CDCl_3$) δ 6.4–5.7 (m, 3 H), 3.0–0.8 (m, 16 H), 0.01 (s, 9 H); mass spectrum, m/e 236 (too small to determine accurate mass), 221 (loss of a methyl group), 122. A second band (R_f 0.1) proved to be recovered starting material (15 mg, 30%).

1,3-Cyclododecadiene. 2-(Trimethylsilyl)cyclododeca-1,3-diene (**40**; 50 mg, 0.20 mmol), *p*-toluenesulfonic acid (38 mg, 0.20 mmol), and dry benzene (2 mL) were refluxed together for 1 h, cooled, and diluted with ether. The solution was extracted with saturated sodium bicarbonate solution (2 × 5 mL) and brine before being dried. The crude oil, obtained in quantitative yield, had an infrared spectrum identical with that of an authentic sample: ^{1}H NMR ($CDCl_3$) δ 6.6–5.1 (m, 4 H), 2.3–1.7 (m, 4 H), 1.7–0.7 (m, 12 H); ν_{max} (film) 3010, 2940, 2870, 1470, 1450, 983, 951 cm^{-1}; mass spectrum, m/e calcd 164.1565, obsd 164.1568.

Acknowledgment. This research was made possible by the generous financial support of the National Cancer Institute (Grant No. CA-12115) and the Eli Lilly Co.

Registry No. **1**, 63031-68-5; **3**, 66228-00-0; **4**, 591-24-2; **5**, 66227-97-2; **6**, 66255-12-7; **7**, 66255-13-8; **8**, 66227-98-3; **9**, 66228-07-7; **10**, 60640-81-5; **11**, 66228-04-4; **12**, 66228-04-4; **13**, 73872-59-0; **15**, 73872-60-3; **17**, 71352-17-5; **19**, 21378-21-2; **21**, 71352-20-0; **22**, 71352-19-7; (*E*)-**36**, 71352-24-4; (*Z*)-**36**, 71352-23-3; (*E*)-**38**, 6221-49-4; (*Z*)-**38**, 41513-26-2; (*Z,E*)-**40**, 73891-28-8; (*Z,Z*)-**40**, 73872-61-4; (*Z,E*)-**41**, 1129-92-6; (*Z,Z*)-**41**, 38772-93-9; 6-(trimethylsilyl)spiro[4.5]dec-6-ene, 66227-87-0; spiro[4.5]decan-6-one benzenesulfonylhydrazone, 66227-81-4; 3-(trimethylsilyl)cholestan-2-ene, 66227-91-6; (*E*)-4-(trimethylsilyl)hept-3-ene, 61892-25-9; (*E*)-4-(trimethylsilyl)-3,4-epoxyheptane, 73872-62-5; 6,7-epoxy-6-(trimethylsilyl)spiro[4.5]decane, 66227-93-8; 1-(trimethylsilyl)-2-isopropyl-5-methyl-7-oxabicyclo[4.1.0]heptane, 66227-94-9; 4,5-benzo-1-(trimethylsilyl)-8-oxabicyclo[5.1.0]oct-4-ene, 66227-95-0; 2β-(trimethylsilyl)-2α,3α-epoxycholestane, 73872-63-6; 4-(trimethylsilyl)-3-heptanal, 66227-99-4; 1-isopropyl-2-(trimethylsilyl)-4-methylcyclohexan-3-ol, 66228-02-2; *cis*-6-(trimethylsilyl)spiro[4.5]decan-7-ol, 73872-64-7; 1,2-benzo-*cis*-5-(trimethylsilyl)cyclohepten-4-ol, 73872-65-8; 3α-(trimethylsilyl)-cholestan-2α-ol, 73924-75-1; 3β-(trimethylsilyl)cholestan-3α-ol, 73872-66-9; 1-(trimethylsilyl)-2-deuterio-4-*tert*-butylcyclohexanol, 73872-67-0; spiro[4.5]decan-7-one, 62788-60-7; spiro[4.5]decan-7-one semicarbazone, 16020-99-8; 3-*tert*-butylcyclohexanone, 936-99-2; 3-heptanone, 106-35-4; carvomenthone, 499-70-7; 1,2-benzocyclohepten-4-one, 34663-15-5; 1,2-benzocyclohepten-4-one 2,4-dinitrophenylhydrazone, 73872-68-1; cholestan-2-one, 16020-93-2; cholestan-3-one, 15600-08-5; 2-(trimethylsilyl)-3-methylcyclohexanone, 73872-69-2; β-tetralone, 530-93-8; 1-(trimethylsilyl)-3,4-dihydronaphthalene, 61892-23-7; 4-methoxy-β-tetralone, 73872-70-5; 2-(trimethylsilyl)cyclohex-2-enol, 71352-18-6; (*E*)-4-(trimethylsilyl)hept-4-en-3-ol, 71352-22-2; (*Z*)-4-(trimethylsilyl)hept-4-en-3-ol, 71352-21-1; 4,5-benzo-1-(trimethylsilyl)cyclohepta-1,4-diene, 66227-89-2; 5,6-benzo-2-(trimethylsilyl)cyclohepta-2,5-dien-1-ol, 71352-25-5; 4,5-benzocyclohepta-2,4-dienol, 71352-26-6; 3-phenyl-2-(trimethylsilyl)-propen-3-ol, 51666-96-7; 5-*tert*-butylcyclohex-2-enol, 32591-15-4; cyclohex-2-enol, 822-67-3; (*E*)-hept-4-en-3-ol, 35077-65-7; (*Z*)-hept-4-en-3-ol, 35077-66-8; 5,6-benzocyclohepta-1,5-dien-3-ol, 71352-27-7; 1-(trimethylsilyl)-3-methyl-6-isopropylcyclohexene, 66227-88-1; 1-(trimethylsilyl)-4-*tert*-butylcyclohexene, 63031-67-4; 1-(trimethylsilyl)-6-methoxy-3,4-dihydronaphthalene, 66227-90-5; 6-methoxy-β-tetralone, 2472-22-2; 1-(trimethylsilyl)cyclohexene, 17874-17-8; 1-(trimethylsilyl)dodecene, 71352-16-4.

(59) The simplest way uncovered with which to work with relatively dry tetra-*n*-butylammonium fluoride was to make a stock solution. This was stored over molecular sieves in acetonitrile under a three-way stopcock.

(60) Magnusson, G.; Thorén, S. *J. Org. Chem.* **1973**, *38*, 1380.

(61) Spectrum identical with that depicted in ref 53, Vol. 1, p 113A.