Silicon in Organic Synthesis. 25. Thermolysis and Desiliconation-Alkylation of [1-(Trimethylsilyl)cyclopropyl]ethylenes as a Route to Spirocyclic Sesquiterpenes[1]

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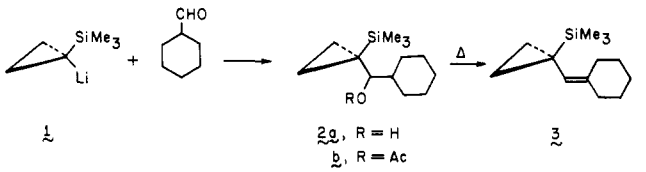
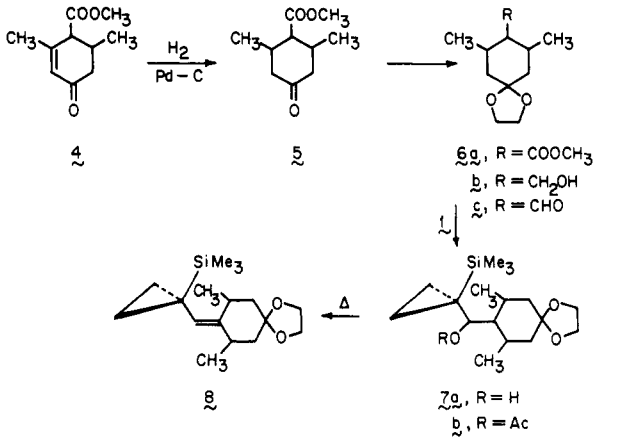
Three routes to [[1-(trimethylsilyl)cyclopropyl]methylene]cyclohexanes and -2-cyclohexenes have been developed. The condensations of [1-(trimethylsilyl)cyclopropyl]lithium with cycloalkyl carboxaldehydes and of α-lithio selenides with 1-(trimethylsilyl)cyclopropanecarboxaldehyde (**10**) are useful and complementary methods for gaining access to the methylenecycloalkanes. For more highly unsaturated systems, the methodology involving titanium(0)-promoted coupling of **10** to cyclic α,β-unsaturated ketones is preferred. Silylcyclopropane **26** has been transformed into the racemic forms of α-vetispirene, hinesol, and β-vertivone. Its broad utility resides in the ease with which desiliconation-alkylation of this substrate can be effected and the high regioselectivity of new carbon-carbon bond formation. Additionally, thermal rearrangement of the trimethylsilyl, (methoxydimethyl)carbinyl, and cyano derivatives invariably proceeds with preferential recombination of the respective biradical intermediate from that surface which is less sterically congested. As a result, the product mixtures are dominated by those stereoisomers suited for elaboration into the spirovetivane sesquiterpenes.

Interest in the development of new syntheses of spirovetivane sesquiterpenes[2] continues unabated. Because stereoselective construction of the spiro[4.5]decane carbon framework and regioselective introduction of at least one double bond comprise the essential elements of any successful approach, these requirements serve as an effective testing ground of new methodology. The feasibility of deploying preparative techniques involving nucleophilic cyclization,[3] electrophilic cyclization,[4] photochemical cycloaddition[5] or rearrangement,[6] carbenic processes,[7] and thermal cyclization[8] has been demonstrated.[9] In the latter category, the intramolecular ene reaction has been utilized to great advantage as a means of attaining acceptable levels of stereocontrol during five-ring closure.[8a-d] Comparable spiroannulation by pyrolysis of suitably constructed vinylcyclopropanes has not been examined. In the course of studies designed to develop the possibly unique advantages offered by 1-(trimethylsilyl) substituted cyclopropanes,[1,10] we have investigated their potential in the

Scheme I



Scheme II



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(6) For example: (a) Marshall, J. A.; Johnson, P. C. *J. Chem. Soc. D* **1968**, 391. (b) Caine, D.; Doucugnani, A. A.; Chao, S. T.; Dawson, J. B.; Ingwalson, P. F. *J. Org. Chem.* **1976**, *41*, 1539. (c) Piers, E.; Worster, P. M. *J. Am. Chem. Soc.* **1972**, *94*, 2895. (d) Williams, J. R.; Sarkisian, G. M. *J. Chem. Soc. D* **1971**, 1564; *J. Org. Chem.* **1972**, *37*, 4463.

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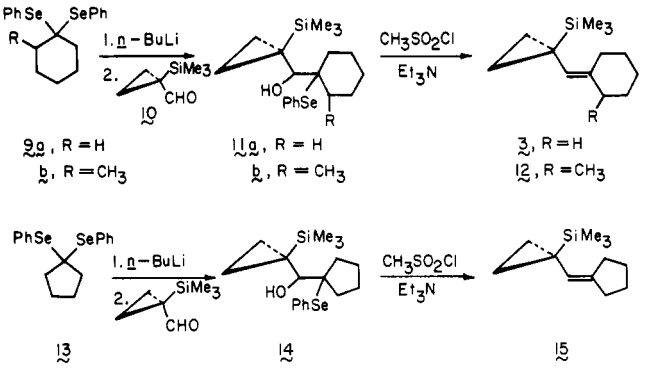
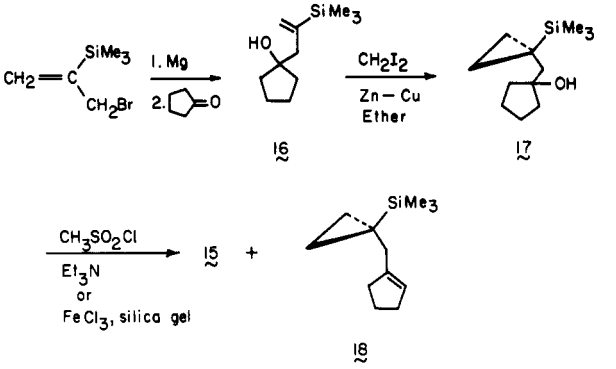
Scheme III



Scheme IV



stereocontrolled construction of spirocyclic compounds. Herein we report a protocol for efficient entry to several [4.5]spirobicyclic sesquiterpenes,[11] which highlights new desiliconation–alkylation or cyanation sequences of potentially wide applicability.

Condensation Reactions Involving [1-(Trimethylsilyl)cyclopropyl]lithium. In order to test the feasibility of our conceptual approach, methods for the efficient construction of [[1-(trimethylsilyl)cyclopropyl]-methylene]cyclohexanes first had to be developed. Initially, the route involving condensation of the bifunctional organometallic reagent **1**[10c] with suitable aldehydes was examined. Whereas treatment of cyclohexanecarboxaldehyde with **1** provided secondary alcohol **2a** in high yield (Scheme I), all attempts to dehydrate this product were unsuccessful. This finding stands in sharp contrast to the ease with which structurally related tertiary alcohols eliminate water.[10] This complication was bypassed by conversion of **2a** to its acetate (**2b**) followed by thermal extrusion of acetic acid at 530 °C in the vapor phase. These conditions delivered **3** in 41% purified yield.

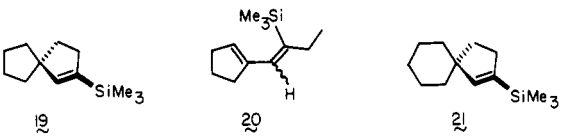
The success accompanying these initial efforts encouraged us to attempt application of this methodology to acquisition of the more complex substrate **8** (Scheme II). To this end, the readily available **4**[12] was catalytically hydrogenated to give **5** which was transformed by conventional means to **6c**. Condensation of this intermediate with **1** proved once again to proceed efficiently. Comparable problems with dehydration required utilization of the acetate pyrolysis process. As before, extensive chromatography was necessary to arrive at pure **8** (31%).

Reaction of α-Lithio Selenides with 1-(Trimethylsilyl)cyclopropanecarboxaldehyde. Although **3** and **8** were in hand, we sought to implement an alternative synthesis which would avoid the necessity of lengthy and tedious purification. The new approach was predicated on the high nucleophilicity of α-lithio selenides, the convenient accessibility of aldehyde **10**,[1] and the regiosepecific manner in which β-hydroxy selenides undergo elimination.[13,14] The wide range of available lithium reagents and mildness of the reaction conditions are additional advantages. The bis selenoketals **9a**, **9b**, and **13** (Scheme III) were prepared by applying Krief's method[14c] to the corresponding cyclic ketones. Individual exposure of these substances to 1 equiv of *n*-butyllithium in tetrahydrofuran solvent at −78 °C, followed by the addition of **10**, gave **11a**, **11b**, and **14** in 81–88% yield. Subsequent reductive elimination was achieved by adding 3 equiv of methanesulfonyl chloride to dichloromethane solutions of the β-hydroxy selenides containing 6 equiv of triethylamine. This procedure allowed for convenient isolation of the vinylcyclopropanes in a pure state. Moreover, careful examination of the reaction mixtures failed to reveal any trace of double-bond isomers. This point is noteworthy in connection with an alternative protocol based upon dehydration reactions involving **17** that invariably led to mixtures of **15** and internal olefin **18** (Scheme IV).

Pilot Thermolysis Experiments. The presence of a trimethylsilyl group at C-1 of a vinylcyclopropane has previously been shown to exert important kinetic consequences.[10] The electropositive character of this substituent so retards the bond reorganization that slower isomerization rates apply. To offset this influence, higher temperatures are necessary to achieve useful levels of conversion to product.

The extent to which such isomerizations are retarded by the 1-trimethylsilyl group can be estimated by the increase in activation energy. For **3** and **15**, the E_a was approximated by assuming an upper limit of 1 s for their half-life at 580 °C and by using a suitable value for the frequency factor. Following an empirical search of vinylcyclopropane reaction parameters,[15] a value of $10^{14.3}$ was settled on. On this basis, the E_a for rearrangement of **3** or **15** is estimated to be approximately 60 kcal/mol. This value, which is likely a higher limit, reflects a 10 kcal/mol increase in E_a due to the 1-trimethylsilyl group.

At the experimental level, passage of **3** and **15** in the gas phase at 30–40 torr (argon as the carrier gas) through a quartz chip-packed tube (30 cm in length) required heating to 580 °C to achieve preparatively useful levels of structural isomerization. The product mixture from **15** consisted of **19** (55–60%) and a diene tentatively formulated as **20** (20%). Under the same conditions, **3** was converted



to **21** (55–60%) and to a mixture of polyolefinic compounds. The latter reaction was noted to be particularly sensitive to small temperature changes which invariably proved deleterious to the formation of **21**. These findings implicate a biradical mechanism wherein hydrogen atom

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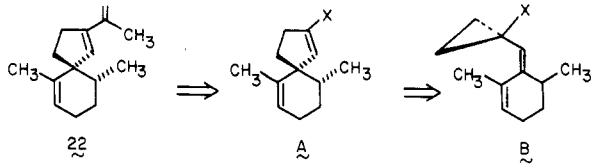
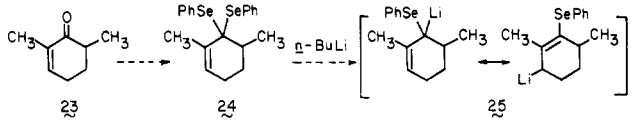
(15) (a) Frey, H. M.; Walsh, R. *Chem. Rev.* **1969**, *6*, 103. (b) Dewar, M. J. S.; Fonken, G. J.; Kirschner, S.; Minter, D. W. *J. Am. Chem. Soc.* **1974**, *96*, 6750. (c) Trost, B. M.; Scudder, P. H. *J. Org. Chem.* **1981**, *46*, 506.

Scheme V



Scheme VI



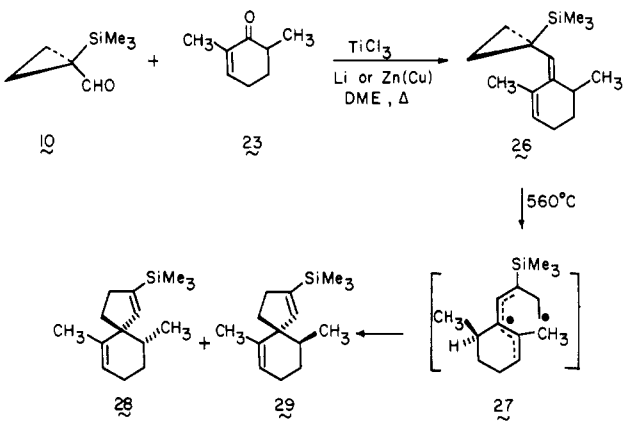
transfer is feasible because of structurally enforced proximity.[16] The flanking methyl groups in **8** proved especially unfavorable to its vinylcyclopropane → cyclopentene rearrangement. At no time was a product corresponding to **19** or **21** observed. Clearly, steric congestion of this magnitude had to be avoided.

The Titanium(0) Coupling Approach. The preceding findings convinced us that the preparation of spirovetivane sesquiterpenes was likely to be realized starting from 1-(trimethylsilyl)cyclopropane derivatives. The difficulties encountered with increased substitution on the terminal vinyl carbon were not an issue since retrosynthetic considerations (Scheme V) surrounding α-vetispirene (**22**), for example, depended on the availability of less sterically encumbered vinylcyclopropanes of type B. Ultimately, our plans called for deployment of a chemoselective Friedel–Crafts acylation of A (X = $SiMe_3$) as the means for introducing an acetyl group in the penultimate step.[17] Wittig olefination would complete the synthesis.

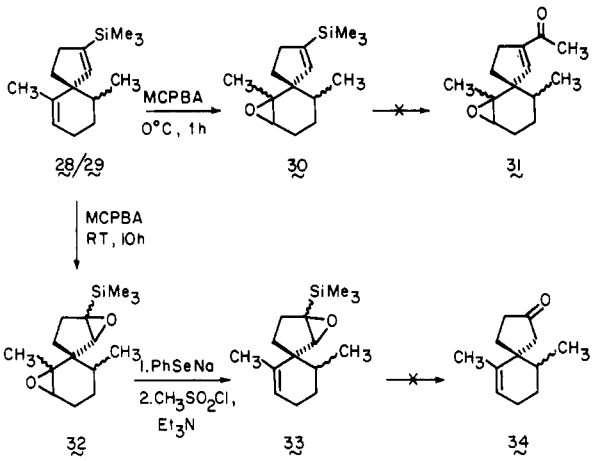
Our selection of **26** as an appropriate starting material posed an immediate problem. The application of α-lithio selenide chemistry was flawed because of an intrinsic inability to convert **23** to **24** without concurrent 1,4-addition (Scheme VI). Additionally, should **25** prove accessible, control of regioselectivity in its reaction with aldehyde **10** appeared problematical. Consequently, attention was turned to a fundamentally different approach.

Recently, three separate research groups have independently observed that a low-valent titanium reagent ($TiCl_4/Zn$,[18] $TiCl_3/Mg$,[19] $TiCl_3/LiAlH_4$[20]) reductively dimerizes ketones and aldehydes to olefins. Although intermolecular couplings work best when two identical carbonyl substrates combine to give a symmetrical product, unsymmetrical couplings have also been successfully carried out in certain cases. The unsymmetrical coupling of an unsaturated ketone with a saturated carbonyl partner was noted to be particularly efficient.[21] McMurry and Krepski have suggested that nucleophilic addition of a stabilized dianion to a free ketone might well be general for mixed reactions in which one component was much more easily reduced than the other.[22] These considerations suggested that unsymmetrical coupling of **23**[23] with

Scheme VII



Scheme VIII



10 might well serve as a preparatively useful synthesis of silylvinylcyclopropane **26**.

Indeed, reaction of **10** with **23** in the presence of the Ti(0) reagent generated by reduction of $TiCl_3$ with zinc–copper couple (or lithium metal) did provide **26** in 50–60% yield (Scheme VII).[24] The 300-MHz ^1H NMR spectrum of **3** (in C_6D_6) clearly revealed it to be a single stereoisomer; preference is given to the less sterically hindered candidate. However, unequivocal distinction has not been made nor is it ultimately relevant.

Subjection of **26** to pyrolysis as described above again required a relatively high temperature (560 °C) to achieve the desired rearrangement. Under these conditions, smoothly efficient bond reorganization occurred to yield a 4:1 mixture of the spirocyclic vinylsilanes **28** and **29**. The configurational assignments rest upon the level of deshielding experienced by the C-10 methyl group in **28** (δ 0.99) relative to that in **29** (δ 0.92) as a result of its spatial proximity to the vinylsilane moiety. The dominance of **28** signaled preferential recombination of biradical **27** from that surface of the six-membered ring which is less sterically encumbered.[8f]

The stage was now set for introduction of the three remaining carbon atoms. Various attempts to acylate **28** chemospecifically at its vinylsilane center under Friedel–Crafts conditions[17] failed, presumably because of competitive attack at the bridgehead cyclohexene double bond. Similarly, exposure to bromine, iodine, cyanogen bromide,

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(23) Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887.
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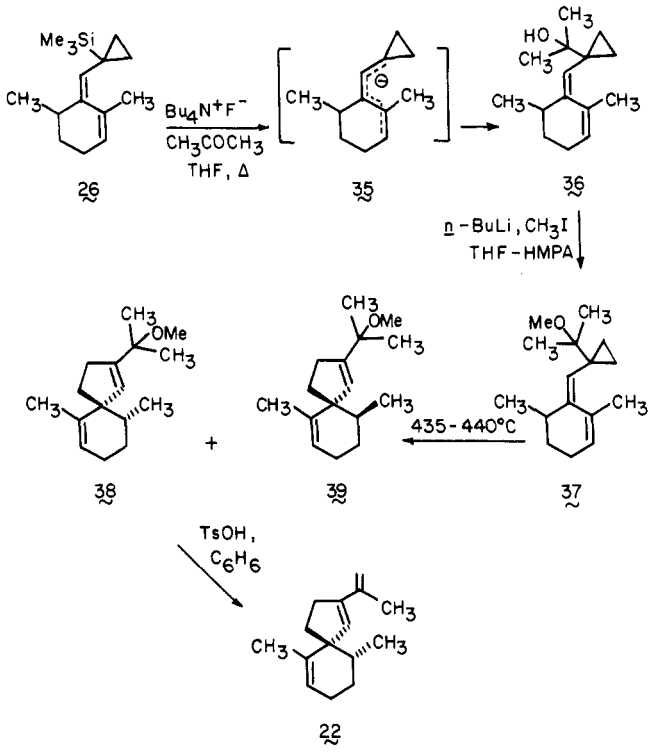
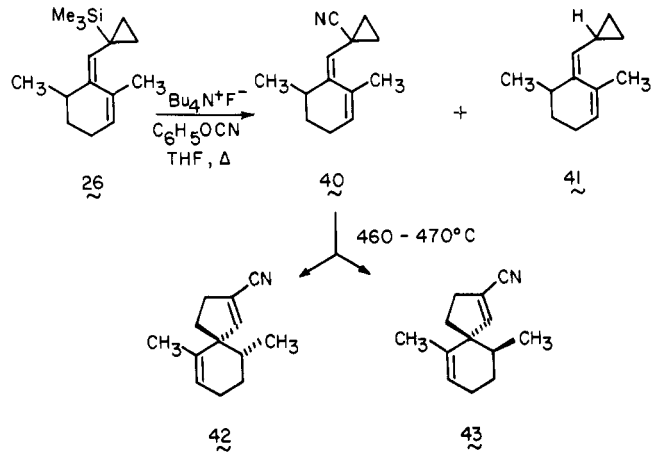
Scheme IX



Scheme X



and dichloromethyl methyl ether–$TiCl_4$[25] led only to formation of tarry products. The observation that epoxidation could be controlled to give **30** (Scheme VIII) led us to undertake acylation studies on this intermediate as well. In no instance did a reaction product exhibit any carbonyl absorption.

Since α,β-epoxy silanes can be converted into carbonyl compounds,[26] the synthesis of **33** was pursued as a possible route to **34**. To this end, epoxidation of **28**/**29** with 2–3 equiv of *m*-chloroperbenzoic acid in dichloromethane solution at room temperature provided **32**. Selective cleavage of the cyclohexyl oxirane ring was accomplished by treating **32** with diphenyl diselenide and sodium borohydride in ethanol.[27] Subsequent reductive elimination[28] of the resulting β-hydroxy selenide as before afforded **33** in 45% overall yield.

A variety of protic and Lewis acid catalysts were screened for their efficacy in transforming this α,β-epoxy silane to **34**.[26] None gave satisfactory results. In related studies, copper-mediated reactions of isopropenylmagnesium bromide and isopropenyllithium[29] with **33** gave no evidence of coupling product formation. These difficulties necessitated that an alternative synthetic approach to an appropriately substituted vinylcyclopropane of type B be designed, where X is some functional group other than trimethylsilyl.

(±)-α-Vetispirene. Efficient replacement of a silicon–carbon bond as in cyclopropane **26** with a carbon–carbon bond constitutes an important problem in organic synthesis. Several prior reports[30] and independent findings in this laboratory[31] suggested the possibility of achieving this goal through preliminary cleavage of the silicon–carbon bond by fluoride ion. In an important first experiment involving **26**, this was effected with anhydrous tetra-*n*-butylammonium fluoride in tetrahydrofuran solution containing acetone at the reflux temperature for 10 h. These conditions served to generate pentadienyl anion **35** which presumably experiences entirely regioselective alkylation at the cyclopropyl carbon atom in order to avoid the development of methylenecyclopropane character. Isomerically pure alcohol **36** was isolated in greater than 90% yield (Scheme IX). Following conversion to methyl ether **37**, thermal rearrangement proved possible at 440 °C and produced a mixture of **38** and **39** (ratio 5:1) in quantitative yield. The heightened stereoselectivity of this reaction, coupled with its efficiency and the ease with which **38** affords (±)-α-vetispirene (**22**), are particularly notable. The overall yield for the five-step conversion of **10** to **22** is 38%.

In harmony with our earlier stereochemical assignments to **28** and **29**, the C-10 methyl doublet in **38** appears at δ 0.85 in C_6D_6 solution. This signal is downfield of that in **39** (δ 0.81) once again because of double-bond anisotropy effects. This trend expectedly carries over to α-vetispirene (δ 0.86) and its C-10 epimer (δ 0.80). The IR and ^1H NMR spectra of our synthetic sesquiterpene proved identical with those supplied to us by Professor Drury Caine.

(±)-Hinesol and (±)-β-Vetivone. The many attractive features of Scheme IX prompted us to determine if its scope could be broadened satisfactorily. In this connection, nitrile **44**, a pivotal intermediate in Buchi's synthesis of (±)-hinesol (**45**) and (±)-β-vetivone (**46**),[3g] was set as a goal. Fluoride-induced desiliconation–canation studies were undertaken with several electrophilic cyanogen-type reagents.[32] Best results were attained when **26** was heated in tetrahydrofuran solution containing 4 equiv of phenyl cyanate[33] and 2–3 equiv of tetra-*n*-butylammonium hydroxide (Scheme X). To allow ready separation of **40** (69%) and **41** (20%) from the triphenyl cyanurate byproduct, the crude reaction mixture was reduced with

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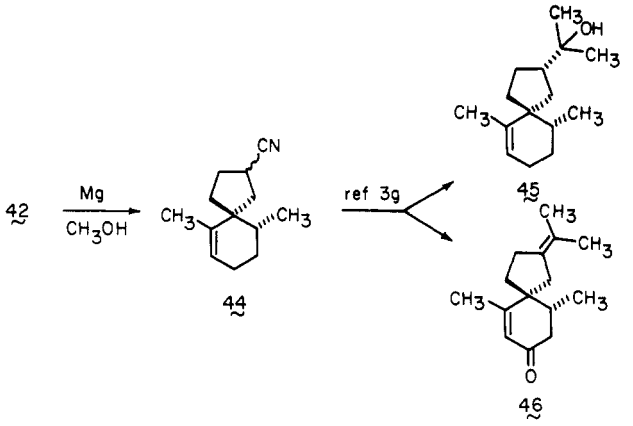
Scheme XI



sodium borohydride in methanol at 0–25 °C prior to workup.

It is noteworthy that the yield of **40** varied considerably with the quality of the tetra-*n*-butylammonium fluoride. Specifically, the activity of the fluoride prepared by drying its paste at 90 °C and 0.5 mm for 24 h was considerably less than that obtained by processing at 130 °C and 0.1 mm for 36 h. Moisture proved to be particularly deleterious, requiring that the hygroscopic fluoride solution be transferred by syringe. Failure to take this precaution resulted in a significant increase in the proportion of **41**, evidently the product of pentadienyl anion protonation.

In keeping with earlier results, thermal rearrangement of **40** gave rise to a mixture of nitriles **42** and **43** in a ratio of 4:1. The respective stereochemical configurations at C-10 follow from the ^{1}H NMR chemical shifts of the methyl doublets (δ 0.99 vs. 0.94 in C_6D_6). Following the isolation of pure **42** by preparative VPC, chemospecific reduction of its conjugated double bond with magnesium in methanol at 0 °C[34] delivered **44** in 20% overall yield from **10** (Scheme XI). The isolation of **44** completes a formal total synthesis of both racemic hinesol (**45**) and racemic β-vetivone (**46**).[3g]

Intermediate silylcyclopropane **26** may well have utility for the synthesis of other members of the spirovetivane family, particularly as new and efficient procedures for replacing carbon–silicon bonds by carbon–carbon bonds becomes available.

Experimental Section

1-[[1-(Trimethylsilyl)cyclopropyl]hydroxymethyl]cyclohexane (2a). Into a solution of 1-bromo-1-(trimethylsilyl)-cyclopropane (1.50 g, 7.76 mmol) in dry tetrahydrofuran (15 mL) cooled to −78 °C was syringed *n*-butyllithium (6.2 mL of 1.5 M in hexane). The resulting light yellow solution was stirred for 3 h before addition of cyclohexanecarboxaldehyde (0.96 g, 8.54 mmol) in tetrahydrofuran (5 mL). The mixture was allowed to warm to room temperature, quenched with a little water, diluted with ether, and washed with saturated ammonium chloride solution prior to drying. Solvent evaporation and purification by MPLC on silica gel (elution with 10% ether in hexane) afforded 1.52 g (86%) of **2a** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.60–1.00 (m, 13 H), 0.60–0.40 (m, 4 H), 0.15 (s, 9 H); MS, *m/e* ($M^+ - CH_5O$) calcd 193.1412, obsd 193.1430; *m/e* ($M^+ - C_6H_{11}$) calcd 143.0892, obsd 143.0894; *m/e* ($M^+ - C_7H_{14}$) calcd 127.0548, obsd 127.0563.

1-[[1-(Trimethylsilyl)cyclopropyl]acetoxymethyl]cyclohexane (2b). To a solution of **2a** (3.0 g, 13.2 mmol) in dry dichloromethane (150 mL) was added 25 mL of triethylamine, 8.6 g (85.3 mmol) of acetic anhydride, and 134 mg (1.1 mmol) of 4-(dimethylamino)pyridine. The reaction mixture was stirred at room temperature for 18 h before being diluted with an equal volume of ether. The organic phase was washed sequentially with 10% aqueous acetic acid, saturated sodium bicarbonate solution, and brine before being dried, filtered, and concentrated. Purification by MPLC on silica gel (elution with 3% ether in hexane) afforded **3b** (3.2 g, 91%) as a colorless oil: IR (neat, cm^{-1}) 3035, 3000, 2915, 2880, 1737, 1450, 1371, 1248, 1016, 972, 933, 837, 754, 685, 650; ^{1}H NMR ($CDCl_3$) δ 3.90 (d, J = 8 Hz, 1 H), 2.00 (s, 3 H), 1.90–0.65 (m, 11 H), 0.45 (m, 4 H), 0.0 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 170.9, 87.6, 42.8, 30.3, 29.8, 26.2, 25.8 (2C), 21.1, 9.0, 8.6, 7.7, 1.4; MS, *m/e* (M^+) calcd 268.1859, obsd 268.1870.

[[1-(Trimethylsilyl)cyclopropyl]methylene]cyclohexane (3). The thermolysis experiment was conducted as previously described[10c] with the following modifications. The quartz tube was not packed with quartz chips and the reaction was conducted at 530 °C and 0.3–0.5 torr with argon as the carrier gas. Flow rates of 6–20 mL/min proved satisfactory. From 1.09 g (4.06 mmol) of **2b**, there was obtained 350 mg (41%) of **3** as a clear colorless oil following MPLC on silica gel (hexane elution) and further purification by VPC (12 ft × 0.25 in. 10% SE-30 on Chromosorb G, 150 °C): IR (neat, cm^{-1}) 3070, 2940, 1250, 840; ^{1}H NMR ($CDCl_3$) δ 5.25 (s, 1 H), 2.20 (m, 4 H), 1.60 (m, 6 H), 0.60 (m, 4 H), 0.0 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 141.5, 125.0, 36.9, 30.0, 28.8, 27.7, 26.9, 11.0 (2C), 7.1, −3.0; MS, *m/e* (M^+) calcd 208.1647, obsd 208.1673.

Anal. Calcd for $C_{13}H_{24}Si$: C, 74.92; H, 11.61. Found: C, 74.90; H, 11.60.

3,5-Dimethyl-4-carbomethoxycyclohexanone (5). Hydrogenation of **4**[12] (4.49 g, 24.6 mmol) in ethyl acetate (200 mL) under 3 atm of hydrogen with 10% Pd on carbon (300 mg) in a Parr apparatus was complete within 15 h at room temperature. Filtration followed by evaporation of solvent left a pale yellow oil that was further purified by distillation to give 4.11 g (91%) of **5** as a colorless liquid: bp 78–88 °C (0.05 torr); IR (neat, cm^{-1}) 2960, 2890, 1760–1670, 1455, 1435, 1350, 1315, 1260, 1220, 1160, 1015, 740; ^{1}H NMR ($CDCl_3$) δ 3.70 (s, 3 H), 2.80–1.95 (m, 7 H), 1.20–0.90 (m, 6 H); MS, *m/e* (M^+) calcd 184.1100, obsd 184.1097.

3,5-Dimethyl-4-carbomethoxycyclohexanone Cyclic Ethylene Acetal (6a). A solution of **5** (3.10 g, 16.8 mmol), ethylene glycol (1.15 g, 18.5 mmol), and pyridiniumm tosylate (0.21 g, 0.84 mmol) in benzene (175 mL) was heated at reflux for 10 h in a Dean–Stark apparatus. The solution was allowed to cool to ambient temperature and washed with 50 mL of saturated brine. The organic phase was dried, filtered, and concentrated to provide the crude product as a colorless liquid. MPLC on silica gel (elution with 10% ether in hexane) gave 3.2 g (85%) of pure **6b**: IR (CCl_4, cm^{-1}) 2960, 2880, 1735, 1460, 1435, 1365, 1320, 1250, 1190, 1170, 1120, 960; ^{1}H NMR ($CDCl_3$) δ 3.90 (s, 4 H), 3.70 (s, 3 H), 2.60–1.20 (m, 7 H), 1.20–0.90 (m, 6 H); MS, *m/e* ($M^+ - 2CH_3$) calcd 197.0814, obsd 197.0788.

3,5-Dimethyl-4-(hydroxymethyl)cyclohexanone Cyclic Ethylene Acetal (6b). To a stirred slurry of lithium aluminum hydride (0.57 g, 14.9 mmol) in dry ether (150 mL) was added dropwise a solution of **6a** (2.72 g, 11.9 mmol) during several minutes. The reaction mixture was gently refluxed for 8 h before being cooled and carefully quenched with ethyl acetate and 20% aqueous sodium potassium tartrate solution. The organic phase was washed with saturated brine, dried, filtered, and concentrated. The crude product was distilled to give 2.19 g (92%) of **6b** as a colorless oil: bp 96–98 °C (0.05 torr); IR (neat, cm^{-1}) 3390, 2930, 2880, 1455, 1365, 1320, 1230, 1125, 1070, 945; ^{1}H NMR ($CDCl_3$) δ 3.90 (s, 4 H), 3.75 (m, 2 H), 2.05–1.20 (m, 8 H), 1.20–0.90 (m, 6 H); MS, *m/e* (M^+) calcd 200.1412, obsd 200.1429.

Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.95; H, 10.08. Found: C, 66.16; H, 10.13.

3,5-Dimethyl-4-formylcyclohexanone Cyclic Ethylene Acetal (6c). To a stirred solution of pyridine (14.5 mL, 180 mmol) in dry dichloromethane (150 mL) was added 9.0 g (90 mmol) of chromium trioxide in small portions over 10 min. After an additional 15 min, a solution of **6b** (3.0 g, 15 mmol) in dichloromethane (15 mL) was added in one portion. The resulting dark reaction mixture was stirred at room temperature for 2.5 h before being diluted with ether (200 mL) and filtered with suction through Celite. The filtrate was concentrated, diluted again with ether (100 mL), and refiltered. The filtrate was washed with saturated aqueous oxalic acid and sodium bicarbonate solutions (repeatedly until colorless), dried, filtered, and concentrated to

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give a pale yellow residue. Distillation afforded 2.38 g (80%) of **6c** as a colorless oil, bp 82–85 °C (0.05 torr). A mixture of one major and two minor stereoisomers was present by NMR and TLC analysis: IR (CCl4, cm^{-1}) 2960, 2890, 2720, 1730, 1460, 1430, 1365, 1320, 1250, 1220, 1180, 1130, 1075, 1015, 965, 855, 765; ^1H NMR ($CDCl_3$) δ 9.95, 9.80, 9.65 (3d, J = 4 Hz, 1 H), 3.80 (s, 4 H), 2.30–0.70 (series of m, 13 H); MS, m/e ($M^+ - C_2H_4$) calcd 170.0934, obsd 170.0960.

1-[[1-(Trimethylsilyl)cyclopropyl]hydroxymethyl]-2,6-dimethyl-4-(ethylenedioxy)cyclohexane (7a). Reaction of aldehyde **6c** with 1 (1.5 equiv) over 24 h (5 h at −78 °C, then allowed slowly to warm to room temperature) in the predsecribed manner gave a 90% yield of **7a** as a mixture of stereoisomers that was resolved into two separate bands via MPLC chromatography on silica gel (elution with 10% ethyl acetate in hexane). Although each band exhibited spectra (^1H NMR, IR) in full agreement with those anticipated for the desired product, those reported below, as well as subsequent chemical transformations, are for the mixture of pure stereoisomers. The analytical sample was obtained by molecular distillation at 110 °C and 0.05 torr: IR ($CHCl_2$, cm^{-1}) 3620, 3490, 3080, 2955, 1450, 1372, 1253, 1147, 1071, 955, 836; ^1H NMR ($CDCl_3$) δ 3.90 (s, 4 H), 2.92 (d, J = 10 Hz, 1 H), 2.00 (s, 1 H), 1.90–0.73 (series of m, 13 H), 0.73–0.27 (m, 4 H), 0.05 (s, 9 H); MS, m/e ($M^+ - CH_3$) 297.

Anal. Calcd for $C_{17}Hj_{32}O_3Si$: C, 65.32; H, 10.34. Found: C, 65.25; H, 10.38.

1-[[1-(Trimethylsilyl)cyclopropyl]acetoxymethyl]-2,6-dimethyl-4-(ethylenedioxy)cyclohexane (7b). To a solution of **7a** (1.53 g, 4.9 mmol) in dry dichloromethane (60 mL) was added 9 mL of triethylamine, 3.2 g (31.7 mmol) of acetic anhydride, and 50 mg (0.41 mmol) of 4-(dimethylamino)pyridine. The reaction mixture was stirred at room temperature for 18 h before being diluted with an equal volume of ether. The organic phase was washed sequentially with 10% aqueous citric acid, saturated sodium bicarbonate solution, and brine before being dried, filtered, and concentrated. The crude oil was purified by MPLC on silica gel (elution with 8% ethyl acetate in hexane). There was isolated two major bands which together comprised 2.25 g (98%) of **7b**. The low-R_f band was recrystallized from hexane for analysis: mp 98–99 °C; IR (CCl_4, cm^{-1}) 2970, 2900, 1735, 1455, 1379, 1265, 1151, 1127, 1075, 1022, 965, 845; ^1H NMR ($CDCl_3$) δ 5.40 (d, J = 3 Hz, 1 H), 3.90 (s, 4 H), 2.05 (s, 3 H), 2.0–0.80 (m, 13 H), 0.60–0.35 (m, 4 H), 0.0 (s, 9 H); ^1H NMR of oily diastereomer ($CDCl_3$) δ 4.45 (d, J = 10 Hz, 1 H), 3.90 (m, 4 H), 2.05 (s, 3 H), 1.80–0.35 (m, 17 H), 0.0 (s, 9 H); MS, m/e ($M^+ - C_5H_{12}O_2Si$) calcd 222.1620, obsd 222.1654.

Anal. Calcd for $C_{19}H_{34}O_4Si$: C, 64.35; H, 9.68. Found: C, 64.48; H, 9.77.

1-[[1-(Trimethylsilyl)cyclopropyl]methylene]-2,6-dimethyl-4-(ethylenedioxy)cyclohexane (8). Pyrolysis of **7b** (1.78 g, 5.0 mmol) in the manner described above gave 0.46 g (31%) of **8** as a colorless liquid after MPLC on silica gel (elution with 3% ether in hexane). Further purification for analysis was accomplished by VPC (6 ft × 0.25 in. 10% SE-30 on Chromosorb G, 180 °C); IR (CCl_4, cm^{-1}) 3075, 2950, 2880, 1447, 1380, 1285, 1250, 1150, 1100, 1049, 950, 840, 686, 647; ^1H NMR ($CDCl_3$) δ 5.30 (s, 1 H), 3.90 (m, 4 H), 3.30–1.85 (m, 2 H), 1.70 (d, J = 5 Hz, 4 H), 1.35–1.10 (2d, J = 7 Hz, 6 H), 0.85–0.30 (m, 4 H), −0.05 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 145.9, 127.4, 109.6, 64.5, 63.0, 40.7, 40.1, 38.6, 30.6, 23.0, 21.8, 11.5, 9.5, 7.7, 3.0; MS, m/e (M^+) calcd 294.2025, obsd 294.2020.

Anal. Calcd for $C_{17}H_{30}O_2Si$: C, 69.31; H, 10.29. Found: C, 69.38; H, 10.24.

1,1-Bis(phenylseleno)cyclohexane (9a). Cyclohexanone (2.0 g, 20 mmol) was slowly added to a solution of benzeneselenol (6.6 g, 42 mmol) in 30 mL of dry carbon tetrachloride in which was suspended anhydrous zinc chloride (1.36 g, 10 mmol). After 10 h at room temperature, the mixture was diluted with ether (200 mL). The organic phase was washed with 10% hydrochloric acid (10 mL) and saturated sodiumn bicarbonate solution (2 × 50 mL) prior to drying. Solvent evaporation afforded 7.4 g (95%) of **9a**: ^1H NMR ($CDCl_3$) δ 7.9–7.2 (m, 10 H), 2.1–1.2 (series of m, 10 H).

2-Methyl-1,1-bis(phenylseleno)cyclohexane (9b). Treatment of 2-methylcyclohexanone (2.2 g, 20 mmol) with zinc chloride (1.36 g, 10 mmol) and benzeneselenol (6.6 g, 42 mmol) as described above gave 7.5 g (92%) of **9b** as a white solid: mp 68.5–69.5 °C; IR (CCl_4, cm^{-1}) 3050, 2920, 1575, 1470, 1434, 682; ^1H NMR (CCl_4) δ 8.0–7.1 (series of m, 10 H), 2.5–1.0 (series of m, 12 H).

Anal. Calcd for $C_{19}H_{22}Se_2$: C, 55.89; H, 5.43. Found: C, 55.91; H, 5.46.

1,1-Bis(phenylseleno)cyclopentane (13). Treatment of cyclopentanone (840 mg, 10 mmol) with zinc chloride (680 mg, 5 mmol) and benzeneselenol (3.3 g, 21 mmol) as described above gave 3.4 g of **13** as a white solid: mp 74–75 °C (from methanol–pentane, 1:4) (lit.[13b] mp 73–75 °C); ^1H NMR ($CDCl_3$) δ 7.9–7.2 (series of m, 10 H), 2.3–1.5 (series of m, 8 H); MS, m/e (M^+) calcd 381.9738; obsd 381.9732.

Condensation Reactions of 10 with α-Lithio Selenides. General Procedure. To a cold (−78 °C) solution of the selenoketal (1 mmol) in dry tetrahydrofuran (5 mL) was syringed 1 mmol of n-butyllithium in hexane. The resulting light yellow solution was stirred for 30 min before addition of 1.0 mmol of **10**. After 2 h at −78 °C, the reaction mixture was allowed to warm to room temperature, treated with a little water, and diluted with ether (30 mL). The organic phase was washed with brine prior to drying. Solvent evaporation afforded the crude β-hydroxy selenides which were recrystallized from a mixture of hexane (8 mL) and ether (2 mL).

For **11a**: 88% yield; mp 93.5–94.5 °C; IR (CCl_4, cm^{-1}) 3485, 3060, 2930, 1575, 1430, 1245, 830; ^1H NMR ($CDCl_3$) δ 7.71–7.21 (series of m, 5 H), 2.96 (s, 1 H), 2.54 (s, 1 H), 2.32–1.11 (series of m, 10 H), 0.8–0.2 (series of m, 4 H), 0.06 (s, 9 H); MS, m/e (M^+) calcd 382.1231, obsd 382.1239.

Anal. Calcd for $C_{19}H_{30}OSeSi$: C, 59.82; H, 7.93. Found: C, 59.87; H, 7.96.

For **11b**: 83% yield as a mixture of diastereomers which were not separated: mp 99–99.5 °C; IR (CCl_4, cm^{-1}) 3600, 3040, 2920, 1570, 1450, 1240, 830; ^1H NMR ($CDCl_3$) δ 8.0–7.15 (series of m, 5 H), 3.52 and 3.25 (two br s, total 1 H), 2.6–0.6 (series of m, 17 H), 0.25 (s, 9 H); MS, m/e (M^+) calcd 396.1387, obsd 396.1395.

Anal. Calcd for $C_{20}H_{32}OSeSi$: C, 60.74; H, 8.15. Found: C, 60.83; H, 8.17.

For **14**: 81% yield; mp 49–50 °C; IR (neat, cm^{-1}) 3480, 3060, 2950, 1575, 1470, 1430, 1245, 835; ^1H NMR ($CDCl_3$) δ 7.79–7.21 (series of m, 5 H), 3.09 (m, 1 H), 2.57 (br s, 1 H), 2.2–1.5 (series of m, 8 H), 0.75–0.3 (series of m, 4 H), 0.03 (s, 9 H); MS, m/e (M^+) calcd 368.1074, obsd 368.1081.

Anal. Calcd for $C_{18}H_{28}OSeSi$: C, 58.83; H, 7.68. Found: C, 58.84; H, 7.65.

Reductive Elimination of the β-Hydroxy Selenides. General Procedure. To a solution of the β-hydroxy selenide (1 mmol) in 5 mL of dichloromethane was added triethylamine (0.7 mL, 5 mmol). The reaction mixture was cooled to 0 °C, and methanesulfonyl chloride (0.23 mL, 3 mmol) was added slowly by syringe over a 5-min period. The reaction mixture was allowed to warm to room temperature (ca. 3 h), quenched with water, and poured into 100 mL of ether and 10 mL of water. The organic phase was washed successively with 5% hydrochloric acid, saturated sodium bicarbonate solution, and brine prior to drying. Evaporation was followed by preparative MPLC on silica gel (elution with hexane).

For **3**: 78% yield; spectra superimposable on those described above.

For **12**: 75% yield as a mixture of diastereomers which were not separated; IR (CCl_4, cm^{-1}) 3050, 2920, 1360, 1240, 835; ^1H NMR (CCl_4) δ 5.2 (m, 1 H), 3.3–1.2 (series of m, 9 H), 1.10 and 1.04 (two d, J = 8 Hz, total 3 H), 0.68–0.4 (series of m, 4 H), 0.0 (s, 9 H); MS, m/e (M^+) calcd 222.1803, obsd 222.1810.

Anal. Calcd for $C_{14}H_{28}Si$: C, 75.59; H, 11.78. Found: C, 75.61; H, 11.73.

For **15**: 80% yield; IR (CCl_4, cm^{-1}) 3060, 2950, 1430, 1245, 835; ^1H NMR (CCl_4) δ 5.3 (m, 1 H), 2.4–2.0 (series of m, 4 H), 1.8–1.4 (series of m, 4 H), 0.2 (s, 4 H), −0.08 (s, 9 H); MS, m/e (M^+) calcd 194.1490, obsd 194.1495.

Anal. Calcd for $C_{12}H_{22}Si$: C, 74.14; H, 11.41. Found: C, 74.18; H, 11.42.

1-[2-(Trimethylsilyl)-2-propenyl]cyclopentanol (16). To a well-stirred slurry of magnesium chloride (3.0 g, 30 mmol) in dry tetrahydrofuran (20 mL) was added potassium (2.1 g, 57 mmol) in pieces. The reaction mixture was heated at reflux for 4 h and recooled to 0 °C. A solution of 2-(trimethylsilyl)-3-bromopropene (1.94 g, 10 mmol) in 5 mL of anhydrous tetra-

hydrofuran was added dropwise during 10 min, and the reaction mixture was stirred at 0 °C for 30 min before being treated with a solution of cyclopentanone (0.67 g, 8 mmol) in tetrahydrofuran (2 mL). After 1 h at 0 °C, the mixture was allowed to warm to 25 °C, treated with 15 mL of water, and diluted with 200 mL of ether. The organic phase was separated, washed with water, dried, and concentrated in vacuo. Chromatography on silica gel (elution with 5% ether in hexane) gave 1.44 g (90%) of **16** as a colorless oil: IR (neat, cm^{-1}) 3840, 2980, 1245, 835; ^1H NMR (CCl_4) δ 5.7 (m, 1 H), 5.5 (d, J = 3 Hz, 1 H), 2.44 (m, 2 H), 2.0–1.4 (series of m, 8 H), 1.24 (s, 1 H), 0.2 (s, 9 H).

Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.19. Found: C, 66.23; H, 11.39.

1-[[1-(Trimethylsilyl)cyclopropyl]methyl]cyclopentanol (17). To a slurry of diiodomethane (1.0 g, 3.75 mmol) and zinc–copper couple (0.65 g) in dry ether (20 mL) was added **16** (0.25 g, 1.25 mmol). The reaction mixture was heated at reflux for 12 h, cooled to 0 °C, treated with saturated ammonium chloride solution, and diluted with ether (100 mL). The separated organic phase was washed with saturated sodium bicarbonate and sodium bisulfite solutions and water prior to drying. Solvent evaporation and chromatography of the residue on silica gel (elution with hexane–ether, 8:1) gave 0.25 g (95%) of **17** as a clear, colorless oil; IR (neat, cm^{-1}) 3460, 3060, 2950, 1245, 835; ^1H NMR (CCl_4) δ 1.8–1.1 (series of m, 11 H), 0.57–0.38 (series of m, 4 H), 0.10 (s, 9 H).

Anal. Calcd for $C_{14}H_{24}OSi$: C, 67.85; H, 11.39. Found: C, 68.25; H, 11.28.

Thermolysis of 15. A 97 mg (0.5 mmol) sample of **15** was passed slowly through a 30-cm-long quartz chip-packed tube at 580 °C in stream of argon (6 mL/min) at 35 torr. The pyrolysate was collected in a U tube immersed in a dry ice–isopropyl alcohol bath. There was obtained 80 mg of a yellow liquid that consisted of **19** and **20**. The two components (ratio ca. 3:1) were separated by preparative VPC at 145 °C (12 ft × 0.25 in. 30% SE-30). There was isolated 58 mg (60%) of **19**: IR (CCl_4, cm^{-1}) 2945, 1585, 1245, 839; ^1H NMR (CCl_4) δ 5.62 (t, J = 2 Hz, 1 H), 2.3 (m, 2 H), 1.9–1.2 (series of m, 8 H), 0.05 (s, 9 H); MS, m/e (M^+) calcd 194.1490, obsd 194.1495.

Anal. Calcd for $C_{12}H_{22}Si$: C, 74.14; H, 11.41. Found: C, 74.25; H, 11.41.

Thermolysis of 3. Heating of **3** (208 mg, 1 mmol) as described above furnished 125 mg (60%) of **21** that was further purified by VPC; IR (CCl_4, cm^{-1}) 2920, 1580, 1245, 835; ^1H NMR (CCl_4) δ 5.68 (t, J = 2 Hz, 1 H), 2.28 (m, 2 H), 1.85–1.21 (series of m, 12 H), 0.05 (s, 9 H); MS, m/e (M^+) calcd 208.1647, obsd 208.1651.

Anal. Calcd for $C_{13}H_{24}Si$: C, 74.92; H, 11.61. Found: C, 74.80; H, 11.94.

(*Z*)-1-[[1-(Trimethylsilyl)cyclopropyl]methylene]-2,6-dimethyl-2-cyclohexene (26). Anhydrous titanium trichloride (2.87 g, 18.6 mmol) was slurried in 30 mL of dry dimethoxyethane under nitrogen, and zinc–copper couple[22] (3.1 g) was added. After 4 h at reflux, the black mixture was cooled and a solution of **10** (0.33 g, 2.3 mmol) and **23** (0.285 g, 2.3 mmol) in 5 mL of dry dimethoxyethane was added over a 5-min period. The mixture was stirred for 3 h at room temperature, heated at reflux for 30 h, cooled to 25 °C, and treated with 100 mL of petroleum ether. The organic layer was decanted from the black residue which was rinsed with petroleum ether (3 × 50 mL). Solvent evaporation and chromatography of the residue on silica gel (elution with hexane) gave 0.3 g (60%) of **26** as a clear, colorless oil; IR (CCl_4, cm^{-1}) 3060, 3010, 2940, 1240, 840; ^1H NMR (CCl_4) δ 5.3 (br s, 2 H), 3.0 (m, 1 H), 2.35–1.58 (series of m, 7 H), 0.9 (d, J = 7 Hz, 3 H), 0.7–0.4 (series of m, 4 H), –0.08 (s, 9 H); MS, m/e (M^+) calcd 234.1803, obsd 234.1810.

Anal. Calcd for $C_{1k}H_{26}Si$: C, 76.84; H, 11.18. Found: C, 76.54; H, 11.12.

Thermolysis of 26. Heating of **26** (234 mg, 1 mmol) at 560 °C in the apparatus described above (nitrogen as carrier gas) afforded 144 mg (70%) of a 6:1 mixture of **28** and **29**: IR (neat, cm^{-1}) 3010, 2940, 1590, 1245, 830; ^1H NMR (C_6D_6) δ 5.86 and 5.64 (two t, J = 1 Hz, total 1 H), 5.5 (br s, 1 H), 2.6–1.6 (series of m, 15 H), 0.99 and 0.92 (two d, J = 7 Hz, total 3 H), 0.08 (s, 9 H); MS, m/e (M^+) calcd 234.1803, obsd 234.1810.

Anal. Calcd for $C_{15}H_{26}Si$: C, 76.86; H, 11.17. Found: C, 77.26; H, 11.12.

6,7-Epoxy-2-(trimethylsilyl)-6,10-dimethylspiro[4.5]dec-1-ene (30). To a cold (0 °C) solution of *m*-chloroperbenzoic acid (270 mg, 1.57 mmol) in dichloromethane (10 mL) was added a solution of crude **28/29** (30 mg, 1.3 mmol) in 2 mL of the same solvent. After 1 h at 0 °C, the reaction mixture was diluted with ether (50 mL) and treated with sodium bisulfite solution (5 mL). The separated organic phase was washed with sodium bicarbonate solution (2 × 5 mL), dried, and concentrated. Preparative thin-layer chromatography on silica gel (elution with hexane–ether, 5:1) gave 250 mg (80%) of **30** as an oil: IR (neat, cm^{-1}) 2950, 1590, 1240, 830; ^1H NMR (CCl_4) δ 5.7 (m, 1 H), 2.8 (m, 1 H), 2.5–1.24 (series of m, 9 H), 1.2 (br s, 3 H), 0.7 (d, J = 7 Hz, 3 H), 0.05 (s, 9 H); MS, m/e (M^+) calcd 250.1752, obsd 250.1744.

Anal. Calcd for $C_{15}H_{26}OS$: C, 71.90; H, 10.45. Found: C, 71.48; H, 10.35.

2-(Trimethylsilyl)-1,2:6,7-diepoxy-6,10-dimethylspiro-[4.5]decane (32). As above, crude **28/29** (160 mg, 0.68 mmol) in 5 mL of dichloromethane was added to a solution of *m*-chloroperbenzoic acid (290 mg, 1.7 mmol) in 15 mL of the same solvent. The reaction mixture was stirred at room temperature for 10 h and worked up in the predescribed manner to give 0.18 (98%) of **32** as a colorless oil: IR (neat, cm^{-1}) 2940, 1245, 835; ^1H NMR (CCl_4) δ 3.0 (s, 1 H), 2.80 (t, J = 2 Hz, 1 H), 2.0–1.2 (series of m, 9 H), 1.08 (s, 3 H), 0.95 (d, J = 7 Hz, 3 H), 0.2 (s, 9 H); MS, m/e (M^+) calcd 266.1701, obsd 266.1710.

Anal. Calcd for $C_{15}H_{26}O_2Si$: C, 67.61; H, 9.84. Found: C, 67.55; H, 9.87.

1,2-Epoxy-2-(trimethylsilyl)-6,10-dimethylspiro[4.5]dec-6-ene (33). To a cold (0 °C) solution of diphenyl diselenide (160 mg, 5.2 mmol) in absolute ethanol (5 mL) was added sodium borohydride (80 mg, 2.2 mmol). The reaction mixture was allowed to warm to room temperature. The resulting clear solution was treated with **32** (220 mg, 0.88 mmol). After 15 h at room temperature, the mixture was treated with water (5 mL) and extracted with ether (2 × 40 mL). The combined organic phases were dried and concentrated. The residue was subjected to reductive elimination as described above. There was isolated 100 mg (45%) of **33** as a clear, colorless oil: IR (neat, cm^{-1}) 2940, 1245, 835; ^1H NMR (CCl_4) δ 5.2 (m, 1 H), 3.0 (s, 1 H), 2.1–1.5 (series of m, 12 H), 1.09 (d, J = 7 Hz, 3 H), 0.09 (s, 9 H); MS, m/e (M^+) calcd 250.1752, obsd 250.1759.

Anal. Calcd for $C_{15}H_{26}OSi$: C, 71.94; H, 10.46. Found: C, 71.47; H, 10.52.

Stock Solution of Tetra-*n*-butylammonium Fluoride. Neutralization of commercial 40% aqueous tetra-*n*-butylammonium hydroxide solution (65 g) with 49% aqueous hydrofluoric acid (ca. 4.1 g) gave tetra-*n*-butylammonium fluoride. Following cooling (10 °C) and filtration, the paste was washed with cold distilled water (2 × 40 mL) and dried at 130 °C and 0.1 torr for 36 h. The resulting hydroscopic mass was dissolved in freshly distilled anhydrous tetrahydrofuran (200 mL).

(*Z*)-1-[[1-(2-Hydroxyprop-2-yl)cyclopropyl]methylene]-2,6-dimethyl-2-cyclohexene (36). To the above stock solution (5 mL) containing 2.5 mmol of active tetra-*n*-butylammonium fluoride was added **26** (234 mg, 1 mmol) and acetone (290 mg, 5 mmol). The reaction mixture was heated at reflux for 10 h, cooled to room temperature, treated with water (10 mL), and diluted with ether (50 mL). The organic layer was separated and the aqueous layer was extracted with ether (2 × 20 mL). The combined organic phases were washed with 5% sodium hydroxide solution (5 mL), water (5 mL), and brine prior to drying. Solvent evaporation and preparative thin-layer chromatography on silica gel (elution with hexane–ether, 4:1) gave 202 mg (90%) of **36** as a clear, colorless oil: IR (neat, cm^{-1}) 3450, 3070, 3005, 2960, 1540, 1360; ^1H NMR (C_6D_6) δ 5.71 (s, 1 H), 5.52 (br s, 1 H), 3.33 (m, 1 H), 2.45–1.57 (series of m, 7 H), 1.25–1.23 (two s, 6 H), 1.08 (d, J = 7 Hz, 3 H), 0.96–0.38 (series of m, 4 H); ^{13}C NMR (C_6D_6) ppm 145.46, 131.99, 125.30, 124.24, 71.71, 29.19, 28.65, 28.41, 28.01, 27.98, 21.96, 20.88, 17.67, 10.58, 9.12; MS, m/e (M^+) calcd 220.1827, obsd 220.1832.

(*Z*)-1-[[1-(2-Methoxyprop-2-yl)cyclopropyl]methylene]-2,6-dimethyl-2-cyclohexene (37). To a cold (–20 °C) stirred slurry of oil-free sodium hydride (72 mg, 3 mmol) in 20 mL of dry tetrahydrofuran was added 5 mL of hexamethylphosphoric triamide folowed by a solution of **36** (440 mg, 2 mmol) in tetrahydrofuran (5 mL). The mixture was allowed to warm to 0 °C

(ca. 10 min), and methyl iodide (430 mg, 3 mmol) was introduced before being allowed to warm to room temperature. After 20 h at 25 °C, the mixture was recooled to 0 °C, treated with 10 mL of water, and diluted with ether (200 mL). The organic phase was washed with water (3 × 10 mL) and brine prior to drying and solvent evaporation. There was obtained 0.47 g (100%) of **37** as a clear, colorless oil: IR (neat, cm^{-1}) 3080, 2960, 1455, 1360, 1150, 1065; ^1H NMR (C_6D_6) δ 5.8 (s, 1 H), 5.5 (br s, 1 H), 3.3 (m, 1 H), 3.1 (s, 3 H), 2.4–1.6 (series of m, 7 H), 1.20 (two s, 6 H), 1.11 (d, J = 7 Hz, 3 H), 0.96–0.43 (series of m, 4 H); ^{13}C NMR (C_6D_6) ppm 144.91, 321.21, 125.04, 124.88, 75.88, 49.33, 29.33, 28.64, 27.80, 22.99, 22.02, 21.73, 20.97, 17.66, 10.35, 9.39; MS, m/e (M^+) calcd 234.1983, obsd 234.1992.

Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.97; H, 10.94.

Thermolysis of 37. Heating of **37** (234 mg, 1 mmol) in the apparatus described above at 435–440 °C (nitrogen as carrier gas) afforded a 5:1 mixture of the spirocyclic compounds **38** and **39** (234 mg, 100%); IR (neat, cm^{-1}) 3005, 2920, 1450, 1360, 1160, 1065; ^1H NMR (C_6D_6) δ 5.33 (br s, 1 H), 5.23 and 5.08 (two t, J = 1 Hz, total 1 H), 3.02 (s, 3 H), 2.35–1.49 (series of m, 12 H), 1.25 (s, 6 H), 0.85 and 0.81 (two d, J = 7 Hz, total 3 H); MS, m/e (M^+) calcd 234.1983, obsd 234.1992.

(±)-α-Vetispirene (22). A 5:1 mixture of **38** and **39** (110 mg, 0.50 mmol) was added to a cold (10 °C) solution of *p*-toluenesulfonic acid (20 mg) in 10 mL of dry benzene. The reaction mixture was allowed to warm to room temperature, stirred for 5 h, and diluted with ether (100 mL). The organic phase was washed with water, sodium bicarbonate solution, and brine prior to drying and solvent evaporation. There was obtained 100 mg (100%) of a 5:1 mixture of **22** and its 10-epimer: IR (neat, cm^{-1}) 3082, 3025, 2960, 2920, 2850, 1630, 1598, 1450, 1370, 874; ^1H NMR (C_6D_6) δ 5.45 (br s, 1 H), 5.32 (m, 1 H), 4.86 (br s, 2 H), 2.50 (m, 2 H), 1.91 (d, J = 1 Hz, 3 H), 1.54 (d, J = 2 Hz, 3 H), 0.86 and 0.80 (two d, J = 7 Hz, total 3 H); MS, m/e (M^+) calcd 202.1721, obsd 202.1726.

The major component, which was obtained in a pure state by preparative VPC (15 ft × 0.25 in. 12% SE-30 on Chromosorb G, 120 °C), exhibited IR and ^1H NMR spectra superimposable on those of an authentic sample of α-vetispirene.

(*Z*)-1-[(1-Cyanocyclopropyl)methylene]-2,6-dimethyl-2-cyclohexene (40). Phenyl cyanate (480 mg, 4 mmol) and **26** (234 mg, 1.0 mmol) were added to an aliquot of the stock solution (10 mL) containing 5 mmol of active tetra-*n*-butylammonium fluoride and the mixture was heated at reflux for 4 h. The resulting deep brown solution was recooled to 25 °C and diluted with ether (50 mL). The organic phase was washed with 5% sodium hydroxide solution, dried, and concentrated. The residue was dissolved in cold (0 °C) methanol (4 mL), and sodium borohydride (115 mg, 3 mmol) was added in small batches while the solution was magnetically stirred. After 2 h at 0 °C, the mixture was treated with water (5 mL) and diluted with ether (50 mL). The organic phase was washed with 5% sodium hydroxide solution (10 mL), dried, and concentrated. Preparative thin-layer chromatography on silica gel (elution with hexane–ether, 5:1) gave 129 mg (69%) of **40** and 32 mg (20%) of **41**.

For **40**: IR (neat, cm^{-1}) 3020, 2920, 2218, 1605, 1440, 1370, 848, 820; ^1H NMR (CCl_4) δ 5.57 (m, 1 H), 5.0 (br s, 1 H), 3.33 (m, 1 H), 2.44–1.6 (series of m, 7 H), 1.53–1.3 (series of m, 2 H), 1.1 (d, J = 7 Hz, 3 H), 1.0–0.77 (series of m, 2 H); MS, m/e (M^+) calcd 187.1360, obsd 187.1365.

Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.15. Found: C, 83.00; H, 9.14.

For **41**: IR (neat, cm^{-1}) 3078, 2920, 1440, 1365, 1187, 950, 830, 805; ^1H NMR (CCl_4) δ 5.39 (m, 1 H), 4.6 (d, J = 10 Hz, 1 H), 3.0 (m, 1 H), 2.43–1.4 (series of m, 7 H), 1.02 (d, J = 7 Hz, 3 H), 0.9–0.3 (series of m, 4 H); MS, m/e (M^+) calcd 162.1408, obsd 162.1412.

Thermolysis of 40. Heating of **40** (187 mg, 1 mmol) in the apparatus described above at 460–470 °C (nitrogen as carrier gas) gave a 4:1 mixture of **42** and **43** (134 mg, 72%): IR (neat, cm^{-1}) 3025, 2980, 2940, 2224, 1620, 1450, 1384, 900; ^1H NMR (C_6D_6) δ 6.26 and 6.12 (two t, J = 1 Hz, total 1 H), 5.68 (br s, 1 H), 2.55 (m, 2 H), 2.2 (m, 2 H), 2.2–1.6 (series of m, 7 H), 1.52 (m, 1 H), 0.99 and 0.94 (two d, J = 7 Hz, total 3 H); MS, m/e (M^+) calcd 187.1360, obsd 187.1365.

Major component **42** was separated by VPC (12 ft × 0.25 in. 5% SE-30 on Chromosorb G, 140 °C) and utilized in the subsequent experiment.

2-Cyano-6,10-dimethylspiro[4.5]dec-6-ene (44). To a solution of **42** (189 mg, 1 mmol) in 15 mL of dry methanol was added (0.96 g, 40 mmol) of magnesium granules. The mixture was stirred for 2 h at 5 °C and 6 h at 25 °C. To the mixture at 0 °C was added 10 mL of 6 N hydrochloric acid over a 15-min period to afford a clear solution. The methanol was evaporated under reduced pressure and the residue was taken up in ether (150 mL). The ether solution was washed with 20 mL of brine, dried, and evaporated to give 1.05 g of oil. Preparative thin-layer chromatography on silica gel (elution with hexane–ether, 8:1) afforded 185 mg (96%) of **44** as a clear, colorless oil: IR (neat, cm^{-1}) 2960, 2223, 1460, 1380, 800; ^1H NMR (CCl_4) δ 5.27 (m, 1 H), 2.61 (m, 1 H), 2.26–1.31 (series of m, 14 H), 0.92 and 0.82 (two d, J = 7 Hz, total 3 H); MS, m/e (M^+) calcd 189.1517, obsd 189.1522.

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Registry No. **1**, 81236-69-3; **(±)-2a**, 91444-88-1; **(±)-2b**, 91444-89-2; **3**, 91444-90-5; **4**, 67333-67-9; **5**, 83194-75-6; **6a**, 91444-91-6; **6b**, 91444-92-7; **6c**, 91444-93-8; **7a**, 91444-94-9; **7b**, 91444-95-0; **8**, 91444-96-1; **9a**, 53198-56-4; **(±)-9b**, 91444-97-2; **10**, 81236-83-1; **(±)-11a**, 91444-98-3; **11b**, 91444-99-4; **(±)-12**, 91445-00-0; **13**, 71518-65-5; **(±)-14**, 91445-01-1; **15**, 91445-02-2; **16**, 91445-03-3; **17**, 91445-04-4; **19**, 91445-05-5; **20**, 91445-06-6; **21**, 91445-07-7; **(±)-22**, 51196-11-3; **(±)-23**, 73723-50-9; **(±)-26**, 91445-08-8; **(±)-28**, 83718-77-8; **(±)-29**, 83718-76-7; **30**, 91445-09-9; **32**, 91445-10-2; **33**, 91445-11-3; **(±)-36**, 91445-12-4; **(±)-37**, 91445-13-5; **(±)-38**, 83718-81-4; **(±)-39**, 83718-80-3; **(±)-40**, 91445-14-6; **(±)-41**, 91445-15-7; **(±)-42**, 91445-16-8; **(±)-43**, 91445-17-9; **44**, 66537-51-7; $CH_2{=}C(SiMe_3)CH_2Br$, 91445-18-0; CH_2I_2, 75-11-6; C_6H_5SeH, 645-96-5; cyclohexanecarboxaldehyde, 2043-61-0; acetone, 67-64-1; (±)-2-methylcyclohexanone, 24965-84-2; cyclopentanone, 120-92-3.