Reductions, Reductive Alkylations, and Intramolecular Cyclizations of Acyl Silanes with Samarium Diiodide or Tributyltin Hydride

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A series of acyl silanes including aliphatic-, aromatic-, and bis-acyl silanes, as well as the acyl silanes bearing other substituents such as a bromine atom and alkenyl, succinimide, and carbonyl groups, were prepared, and their reactions with samarium diiodide or tributylstannane were studied. The reactions of acyl silanes occurred in various manners such as reductions, reductive alkylations, intramolecular radical cyclizations, pinacol couplings, aldol reactions, and Tishchenko reactions, depending on the nature of substrates and reaction conditions. Acyl silanes were generally reduced to give the corresponding α-silyl alcohols without transfer of silyl groups. Intramolecular radical cyclizations of 5-hexenoyl silanes and 1-silyl-1,5-pentanedione were realized to give α-silyl cyclopentanols and 1,2-cyclopentanediol derivatives, respectively. On treatment with samarium diiodide in tetrahydrofuran, 1-(trimethylsilyl)-1,6-hexanedione underwent a pinacol coupling reaction in the presence of *t*-BuOH, whereas it underwent a Tishchenko reaction in the presence of MeOH. The Tishchenko reaction of 1-silyl-1,5-pentanedione gave a *δ*-silyl-*δ*-lactone. On treating with samarium diiodide, 1-(trimethylsilyl)-1,5-hexanedione and 1,5-bis(trimethylsilyl)-1,6-hexanedione, underwent, respectively, intramolecular aldol reactions.

Introduction

Acyl silanes are carbonyl derivatives exhibiting unusual chemical and physical properties.[1] Acyl silanes, though sensitive to light and to basic media, behave frequently as typical ketones such as giving α-silyl alcohols on treatment with $LiAlH_4$[2] or borane[3] and giving hydrazones on treatment with hydrazines.[4] An acyl silane can be considered as the synthetic equivalent of an aldehyde of which hydrogen atom is substituted with a bulky silyl group. For example, addition of organolithium[5] or Grignard reagent[6] to an acyl silane gives the secondary alcohol as a consequence of the Brook rearrangement[7] to form a strong O-Si bond. The reaction of an acyl silane with an α-lithio sulfone[8] gives silyl enol ethers via the Brook rearrangement and extrusion of the sulfonyl group. Metalation of acyl silanes with lithium diisopropylamide[9] or reduction of α-bromoacyl silane with zinc (Reformatsky reaction)[10] give the corresponding enolates, which undergo aldol reactions with aldehydes in diastereoselective manners. Aldol reactions between silyl enol ethers of acylsilanes and acetals are also realized with the catalysis of Lewis acids.[11] Aromatic acyl silanes function as acyl anion equivalents on treating with fluoride ion and are trapped with electrophiles.[12,13] 2-Alkenoyl silanes are generally used as the acceptors in Michael reactions,[14] Diels−Alder reactions,[15] and [3 + 2] annulations.[16] Intramolecular addition of a carbon radical to acyl silane is facilitated by an irreversible radical Brook rearrangement.[17]

In recent years, one-electron reductions of carbonyls with SmI_2 to produce samarium ketyl radical anions have generated a lot of attentions.[18] These ketyl radical intermediates are found useful in the formation of carbon−carbon bonds via addition to multiple bonds[19] or Barbier-type of coupling reactions with halides.[20] When employed intramolecularly, these methods can be used to construct cyclic structures.[21] Similarly, stannyl radicals generated from tributyltin hydride and carbonyl compounds have also been used to generate *O*-stannyl ketyls.[22] These ketyls were shown to add intramolecularly to olefins or carbonyls quite successfully. As part of our interest in the exploration of the radical reactions of acyl silanes, we have studied the reactions of acyl silanes with SmI_2 and tributyltin hydride. Experiments

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(1) For reviews on the chemistry, synthesis, and physical properties of acylsilanes, see: (a) Page, P. C. B.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147. (b) Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647. (c) Cirillo, P. F.; Panek, J. S. *Org. Prep. Proc. Int.* **1992**, *24*, 553.

(2) Brook, A. G. *Adv. Organomet. Chem.* **1968**, *7*, 96.

(3) Buynak, J. D.; Strickland, J. B.; Hurd, T.; Phan, A. *J. Chem. Soc., Chem. Commun.* **1989**, 89.

(4) (a) Yoshida, J.-i.; Itoh, M.; Matsunaga, S.-i.; Isoe, S. *J. Org. Chem.* **1992**, *57*, 4877. (b) Bartoli, G.; Bosco, M.; Dalpozzo, R.; Marcantoni, E. *Tetrahedron Lett.* **1990**, *31*, 6935.

(5) For a representive example, see: Reich, H. J.; Eisenhart, E. K.; Olsen, R. E.; Kelly, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 7791.

(6) For a representive example, see: Kuwajima, I.; Enda, J. *J. Am. Chem. Soc.* **1985**, *107*, 5495.

(7) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.

(8) Reich, H. J.; Eisenhart, E. K. *J. Org. Chem.* **1984**, *49*, 5282.

(9) Schinzer, D. *Synthesis* **1989**, 179.

(10) Horiuchi, Y.; Taniguchi, M.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1995**, *36*, 5353.

(11) Ricci, A.; Degl'Innocenti, A; Borselli, G.; Reginato, G. *Tetrahedron Lett.* **1987**, *28*, 4093.

(12) Degl'Innocenti, A.; Pike, S.; Walton, D. R. M.; Seconi, G.; Ricci, A.; Fiorenza, M. *J. Chem. Soc., Chem. Commun.* **1980**, 1201.

(13) Schnizer, D.; Heathcock, C. H. *Tetrahedron Lett.* **1981**, *22*, 1881.

(14) Danheiser, R. L.; Fink, D. M. *Tetrahedron Lett.* **1985**, *26*, 2509.

(15) Reich, H. J.; Kelly, M. J.; Olson, R. E.; Holtan, R. C. *Tetrahedron* **1983**, *39*, 949.

(16) Danheiser, R. L.; Fink, D. M. *Tetrahedron Lett.* **1985**, *26*, 2513.

(17) (a) Dalton, J. C.; Bourque, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 699. (b) Harris, J. M.; Macinnes, I.; Walton, J. C.; Mailard, B. J. *J. Organometal. Chem.* **1991**, *403*, C25−C28. (c) Tsai, Y.-M.; Cherng, C.-D. *Tetrahedron Lett.* **1991**, *32*, 3515. (d) Curran, D. P.; Jiang, W.-T.; Palovich, M.; Tsai, Y.-M. *Synlett* **1993**, 403. (e) Tsai, Y.-M.; Tang, K.-H.; Jiaang, W.-T. *Tetrahedron Lett.* **1993**, *34*, 1303. (f) Tsai, Y.-M., Ke, B.-W. *J. Chin. Chem. Soc.* **1993**, *40*, 641. (g) Robertson, J.; Burrows, J. N. *Tetrahedron Lett.* **1994**, *35*, 3777. (h) Tsai, Y.-M.; Chang, S.-Y. *J. Chem. Soc., Chem. Commun.* **1995**, 981.

(18) For reviews on SmI_2, see: (a) Kagan, H. B; Namy, J. L. *Tetrahedron* **1986**, *42*, 6573. (b) Inanaga, J. *J. Syn. Org. Chem.* **1989**, *47*, 200. (c) Soderquist, J. A. *Aldrichim. Acta* **1991**, *24*, 15. (d) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29. (e) Brandukova, N. E.; Vygodskii, Y. S.; Vinogradova, S. V. *Russ. Chem. Rev.* **1994**, *63*, 345.

(19) For intermolecular ketyl−olefin coupling reactions, see: Ujikawa, O.; Inanaga, J.; Yamaguchi, M.; *Tetrahedron Lett.* **1989**, *30*, 2837.

(20) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693.

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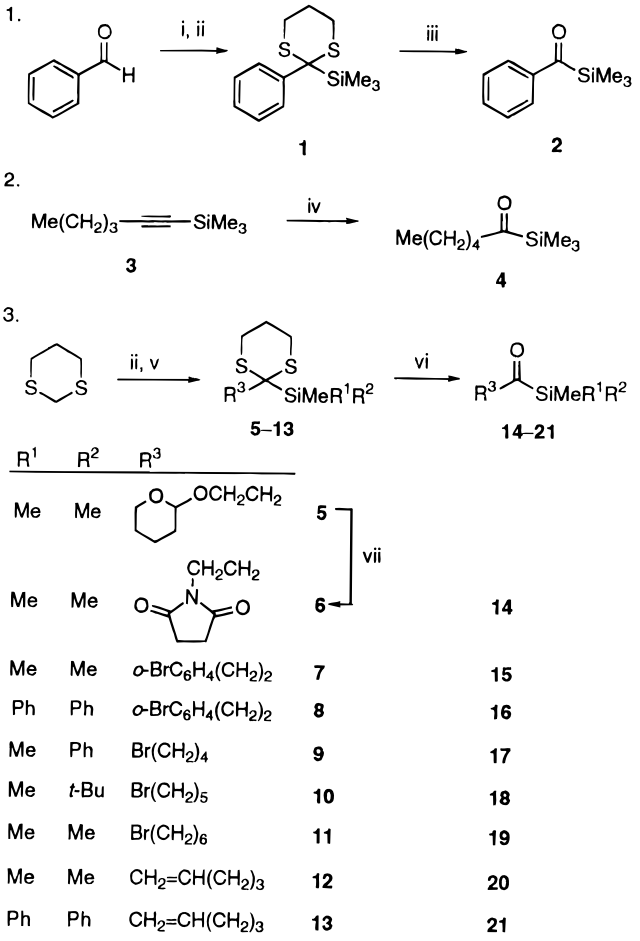
Scheme 1



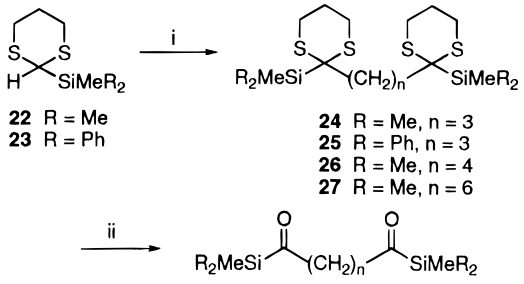
Reagents and conditions: i, $HS(CH_2)_3SH$, cat. $BF_3{\bullet}OEt_2$, $CHCl_3$; 87%. ii, BuLi, $ClSiMeR^1R^2$, THF; for **1**, $R^1 = R^2 = Me$, 98%. iii, HgO, $HgCl_2$, MeOH, H_2O; 82%. iv, $Me_2S{\bullet}BH_3$, THF; Me_3NO; 77%. v, BuLi, R^3X. vi, HgO, $BF_3{\bullet}OEt_2$, THF/H_2O or $(NH_4)_2Ce(NO_3)_6$, CH_3CN/H_2O. vii, cat. TsOH, MeOH; succinimide, Ph_3P, DEAD, THF; 77%.

are designed to examine the reactivities of the silyl substituted ketyls with various functionalities. The results of these experiments are described in this paper.

Results and Discussion

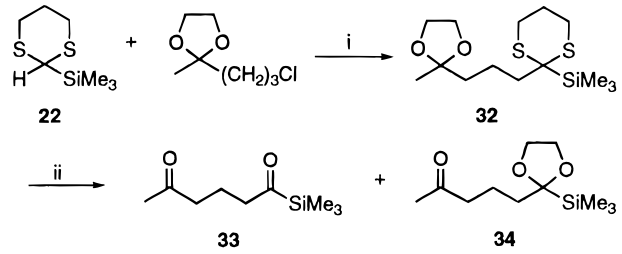
Acyl silanes **2**[23b] and **14**−**21** were generally prepared from 1,3-dithianes (Scheme 1) according to Brook and Corey's method.[23] Hexanoyl silane **4**[24] was prepared from hydroboration−oxidation of 1-hexynyl silane **3**. Preparation of bis-acyl silanes **28**−**31** (Scheme 2), 5-oxohexanoyl silane **33** (Scheme 3), and formylalkanoyl silanes **37** and **46**−**48** (Scheme 4) were also illustrated. Hydrolysis of 2-silyl-1,3-dithianes to the corresponding acyl silanes

Scheme 2



Reagents and conditions: i, BuLi, $Br(CH_2)_nBr$ (0.5 equiv), THF, 0 °C. ii, HgO, $BF_3{\bullet}OEt_2$, THF/H_2O; 61-68% from **22** or **23**.

Scheme 3



Reagents and conditions: i, BuLi, THF, 0 °C; 81%. ii, HgO, $BF_3{\bullet}OEt_2$, THF, H_2O; **33**, 81%; **34**, 13%; or in acetone, H_2O; **33**, 91%.

were generally carried out with $HgO/BF_3{\cdot}OEt_2$ in aqueous THF solution.[25] In addition to the desired acyl silane **33** (81%), a side-product **34** (13%) was obtained from a transacetalation when **32** was hydrolyzed in such conditions. The problem was circumvented by hydrolysis in aqueous acetone solution, giving exclusively **33** in 91% yield. In certain cases, the oxidizing agent $Ce(NH_4)_2(NO_3)_6$[26] or $PhI(CF_3CO_2)_2$[27] were also used for removal of dithiane moiety.

Bis[2-(trialkylsilyl)-1,3-dithianes] **24**−**27**, the precursors of bis-acyl silanes **28**−**31**, were obtained by alkylations of the corresponding 2-(trialkylsilyl)-1,3-dithianes (**22** or **23**) with appropriate dibromides (0.5 equiv). Alkylation of 2-(trimethylsilyl)-1,3-dithiane (**22**) with 1,4-dibromobutane (1 equiv) gave the dithiane **40**, whereas alkylation of 1,3-dithiane with 1,5-dibromopentane (0.5 equiv) afforded the bis-dithiane **41**. Reaction of the bromide **40** with 2-lithio-1,3-dithiane and monosilylation of the bis-1,3-dithiane **41** gave **43** and **44**, which were subsequently hydrolyzed with $HgO/BF_3{\cdot}OEt_2$ to give formylalkanoyl silanes **47** (60%) and **48** (55%). Formylalkanoyl silane **46** was synthesized similarly by monosilylation of the bis-dithiane **39** followed by hydrolysis (70% from **39**). The bis-dithiane **39** was in turn synthesized (55%) from the reaction of 1,3-propanedithiol with glutaraldehyde.[28] Sequential transacetalation (cat. TsOH, Me_2CO) and hydrolysis ($HgO/BF_3{\cdot}OEt_2$) of the dithiane **45**, prepared from **22** and 5-bromopentanal ethylene acetal,[29] also led to the acyl silane **47**. 5-Oxopentanoyl

(21) (a) Molander, G. A.; Kenny, C. *Tetrahedron Lett.* **1987**, *28*, 4367. (b) Fevig, T. L.; Elliott, R. L.; Curran, D. P. *J. Am. Chem. Soc.* **1988**, *110*, 5064. (c) Molander, G. A.; Mckie, J. A. *J. Org. Chem.* **1991**, *56*, 4112.

(22) (a) Beckwith, A. L. J.; Roberts, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 5893. (b) Sugawara, T.; Otter, B. A.; Ueda, T. *Tetrahedron Lett.* **1988**, *29*, 75. (c) Enholm, E. J.; Burroff, J. A. *Tetrahedron Lett.* **1992**, *33*, 1835. (d) Zelechonok, Y.; Silverman, R. B. *J. Org. Chem.* **1992**, *57*, 5785. (e) Rawal, V. H.; Krishnamurthy, V.; Fabre, A. *Tetrahedron Lett.* **1993**, *34*, 2899. (f) Lee, E.; Tae, J. S.; Chong, Y. H.; Park, Y. C. *Tetrahedron Lett.* **1994**, *35*, 129. (g) Hays, D. S.; Fu, G. C. *J. Am. Chem. Soc.* **1995**, *117*, 7283. (h) Enholm, E. J.; Kinter, K. S. *J. Org. Chem.* **1995**, *60*, 4850.

(23) (a) Brook, A. G.; Duff, J. M.; Jones, P. F.; Davis, N. R. *J. Am. Chem. Soc.* **1967**, *89*, 431. (b) Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434.

(24) Miller, J. A.; Zweifel, G. *Synthesis* **1981**, 288.

(25) Vedejs, E.; Fuchs, P. L. *J. Org. Chem.* **1971**, *36*, 366.

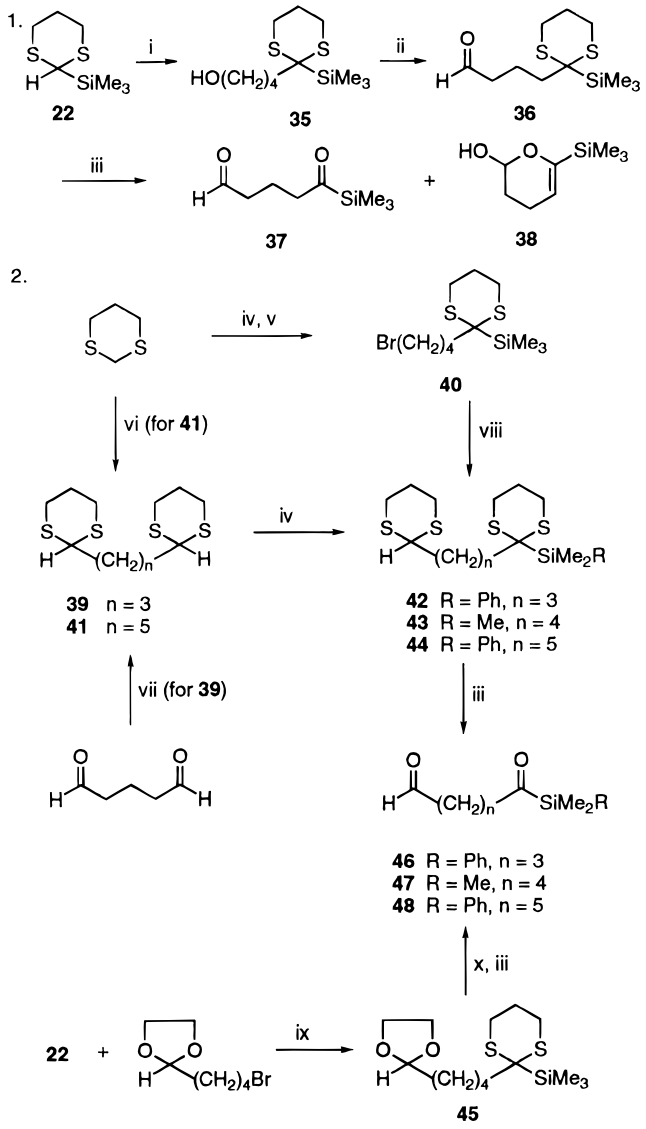
(26) (a) Ho, T.-L; Ho, H. C.; Wong, C. M. *J. Chem. Soc., Chem. Commun.* **1972**, 791. (b) Ho, H. C.; Ho, T.-L; Wong, C. M. *Can. J. Chem.* **1972**, *50*, 2718.

(27) Stork, G.; Zhao, K. *Tetrahedron Lett.* **1989**, *30*, 287.

(28) Corey, E. J.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1077.

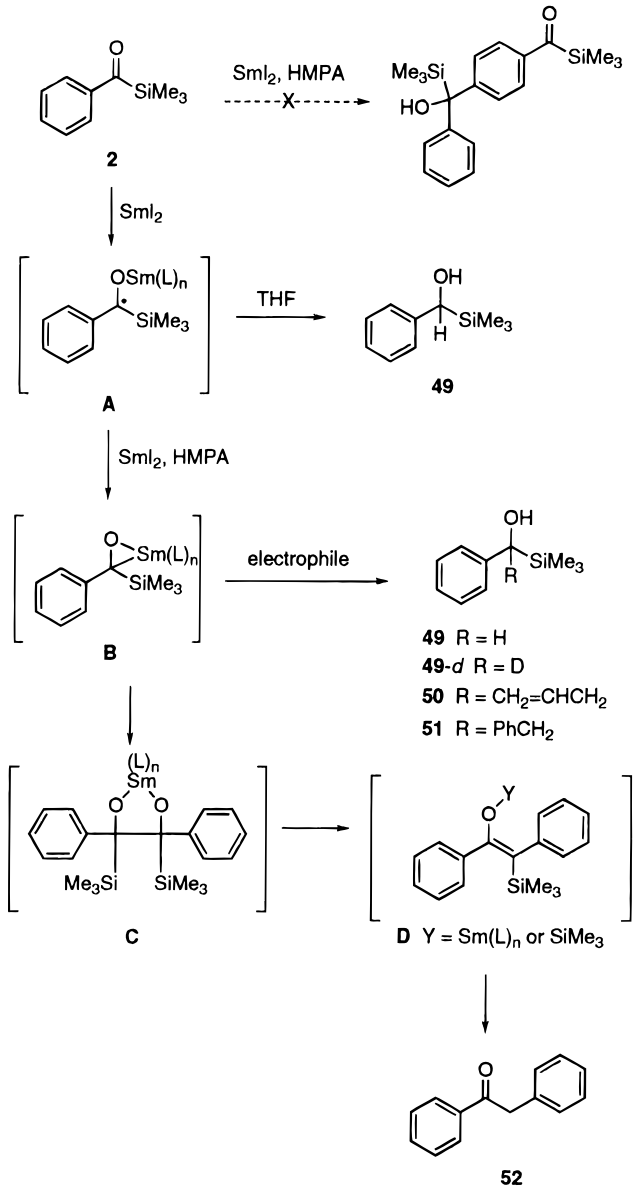
(29) Kulkarni, S.; Patil, V. D. *Heterocycles* **1982**, *18*, 163.

Scheme 4



Reagents and conditions: i, LDA (3.3 equiv), $HO(CH_2)_4Cl$ (2 equiv), THF; 99%. ii, PCC, CH_2Cl_2; 45%. iii, HgO, BF_3•OEt_2, THF, H_2O; **37**, 77%; **38**, 15%. iv, BuLi, RMe_2SiCl, THF. v, BuLi, $Br(CH_2)_4Br$ (1 equiv). vi, BuLi, $Br(CH_2)_5Br$ (0.5 equiv), THF; 76%. vii, $HS(CH_2)_3SH$, BF_3•OEt_2, $CHCl_3$; 55%. viii, 1,3-dithiane, BuLi, THF. ix, BuLi, THF. x, cat. TsOH, Me_2CO.

Scheme 5



silane **37** was prone to undergo intramolecular cyclization to give a dihydropyran derivative **38** if excess of acid existed in the reaction media.[30]

The reaction of benzoyl silane **2** with SmI_2 in THF gave simply the reduction product **49** (63%)[31] even in the absence of proton source. When the reaction was conducted in the presence of HMPA, benzyl phenyl ketone (**52**) was obtained (30%) in addition to the silyl alcohol **49** (47%). Benzaldehyde reacts with SmI_2 in the presence of HMPA to give a phenyl−carbonyl coupling product, 4-(1-hydroxybenzyl)benzaldehyde.[32] Acetophenone follows the similar reaction pathway.[32] However, benzoyl silane did not undergo such phenyl−carbonyl coupling reaction. Treatment of benzoyl silane **2** with SmI_2 in the presence of an electrophile such as *t*-BuOD, allyl bromide, or benzyl bromide gave **49**-*d* (62%) and alkylated products **50** (84%) and **51** (91%). Compound **49**-*d* was characterized by a triplet signal occurring at δ 69.9 (J = 20 Hz) for the carbinyl carbon. The reaction mechanism is shown (Scheme 5). Reduction of the acyl silane by sequential transfers of two electrons from SmI_2 (2 equiv) might form an organosamarium **B**[33] to account for the deuteration and alkylations. Benzyl phenyl ketone might be derived from a pinacolate intermediate **C**[31] via sequential transfers of silyl groups and hydrolysis, though the pinacol corresponding to **C** was not isolated.

Hexanoyl silane **4** was reduced with SmI_2 to give the alcohol **53** (50%). Selective reductions of acyl silanes **14**, **15**, and **16** with SmI_2 were realized, giving **54** (50%), **55** (63%), and **56** (52%), respectively, with intact succinimide and bromophenyl moieties. 5-Bromopentanoyl silane **17** was reduced with SmI_2, followed by the intramolecular alkylation, to give exclusively 1-silylcyclopentanol **57** (47%). The reaction of 6-bromohexanoyl silane **18** gave 1-silylcyclohexanol **58** (45%) and an open-chain alcohol **59** (17%). 7-Bromoheptanoyl silane **19** was simply reduced to the corresponding silyl heptanol **60** (55%),

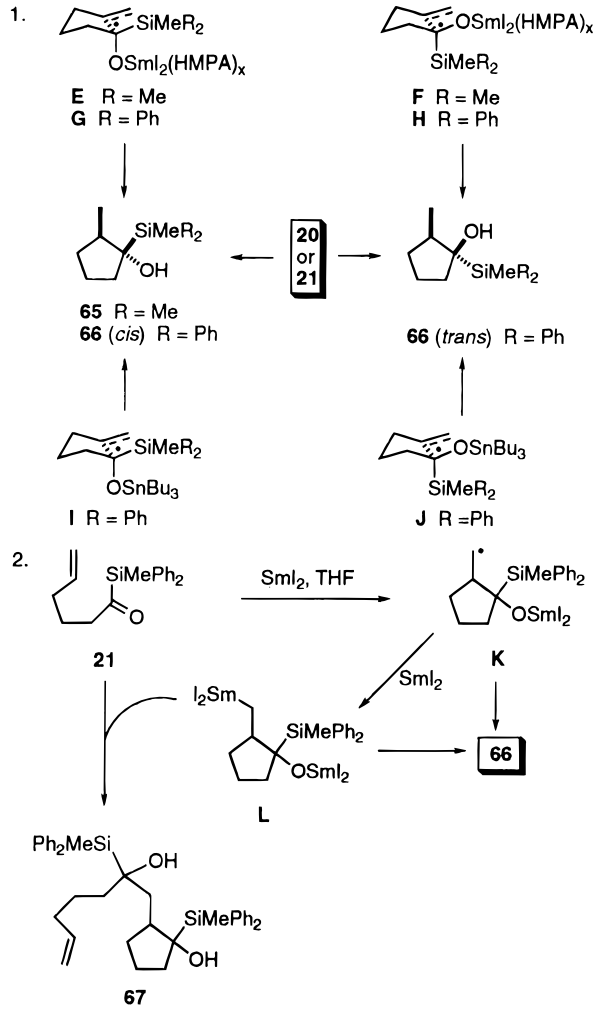
(30) Tsai, Y.-M.; Nieh, H.-C.; Cherng, C.-D. *J. Org. Chem.* **1992**, *57*, 7010.

(31) Taniguchi, Y.; Fuji, N.; Makioka, Y.; Takaki, K., Fujiwara, Y. *Chem. Lett.* **1993**, 1165.

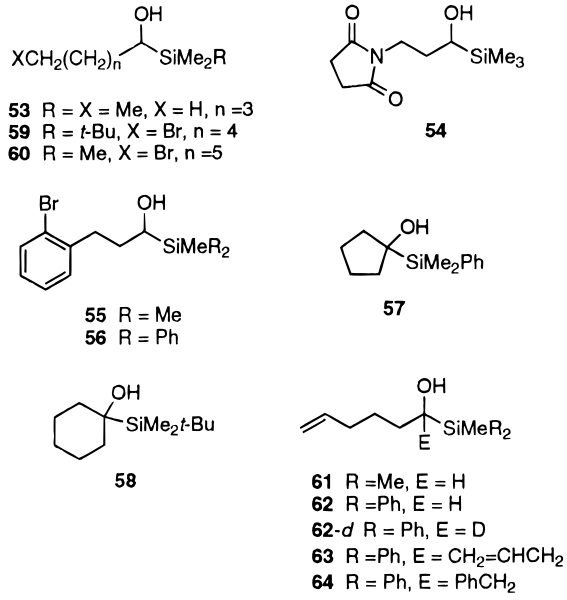
(32) Shiue, J. S.; Lin, C. C.; Fang, J. M. *Tetrahedron Lett.* **1993**, *34*, 335.

(33) (a) Molander, G. A.; Kenny, C. *J. Org. Chem.* **1991**, *56*, 1439. (b) Curran, D. P.; Totleben, M. *J. Am. Chem. Soc.* **1992**, *114*, 6050.

Scheme 6

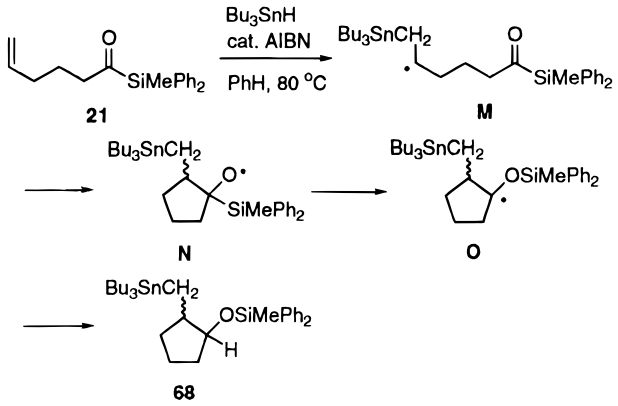


presumably the intramolecular alkylation to form a seven-membered ring was energetically unfavorable.



5-Hexenoyltrimethylsilane (**20**) was treated with SmI_2 in the presence of HMPA (1−2 equiv) and *t*-BuOH (2 equiv) to give the corresponding silyl hexenol **61** (32%) and a silyl cyclopentanol **65** (26%) derived from the intramolecular radical cyclization (Scheme 6). Compound **65** (*cis*-configuration) had the methyl and trimethylsilyl groups on the same face as indicated by the NOE study, *i.e.* irradiation of the Me_3Si signal (at δ 0.08) causing a 22% NOE of the adjacent methyl group (at δ 0.87). The reaction of 5-hexenoylmethyldiphenylsilane (**21**) with SmI_2 in THF/HMPA/*t*-BuOH afforded the silyl hexenol **62** (48%) and the silyl cyclopentanol **66** (32%). The cyclization product **66** existed as two diastereomers, of which the ratio (*cis*/*trans*) varied from 70/30 to 40/60 depending on the amounts of HMPA (1−8 equiv) and *t*-BuOH (1−2 equiv). The reaction in THF/*t*-BuOH (without HMPA) gave more reduction product **62** (52%), accompanied by **66** (38%, *cis*/*trans* = 55:45). The reaction in THF (without *t*-BuOH or HMPA) gave **62** (13%), **66** (18%, *cis*/*trans* = 46:54), and a diol **67** (38%, a mixture of diastereomers). In the presence of allyl bromide or benzyl bromide, the reaction of **21** with SmI_2 gave Barbier-type products **63** (84%) or **64** (79%), no intramolecular cyclization occurred.

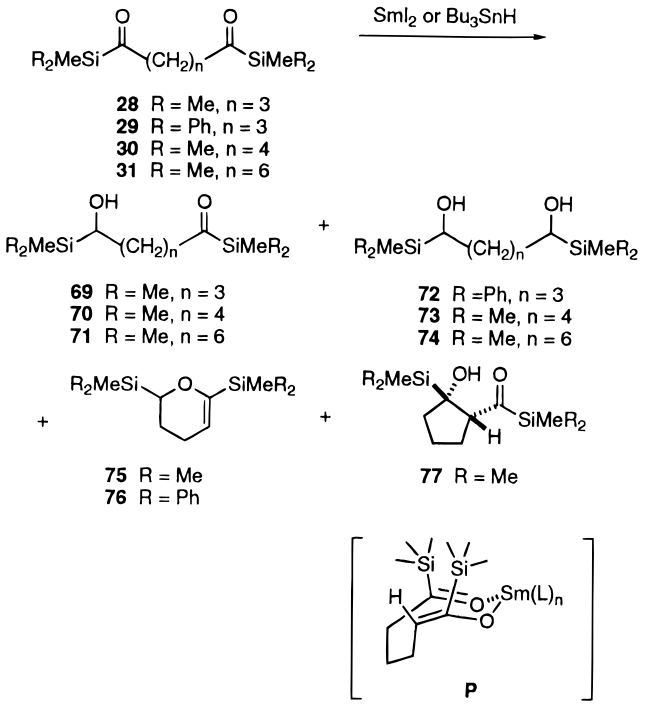
Scheme 7



The reaction of **21** with tributyltin hydride revealed that the cyclization was less efficient. The major product obtained was the uncyclized alcohol **62** (45%). Cyclized alcohol **66** was obtained in 12% as a mixture of *cis*/*trans* (5:1) isomers. Silyl ethers *cis*-**68** (9%) and *trans*-**68** (6%) were also isolated (Scheme 7). These silyl ethers were originated from initial addition of tin radical to the terminal olefin followed by cyclization with the acyl silane.[17c] The stereochemistry of **68** was determined by comparison of the ^1H NMR chemical shifts with those of 2-methyl-1-(methyldiphenylsilyloxy)cyclopentane.[17e] The H-1 resonance of *cis*-**68** had a larger chemical shift (at δ 4.05) than that of *trans*-**68** (at δ 3.74) in agreement with the trend in 2-methyl-1-(methyldiphenylsilyloxy)cyclopentane, *i.e.* the H-1 of *cis*-isomer appearing at δ 4.16 and that of *trans*-isomer appearing at δ 3.77.

On treating with SmI_2 or Bu_3SnH, alkenoyl silanes **20** and **21** having terminal vinyl groups appeared to proceed with similar mechanisms of radical cyclizations (Scheme 6).[34] The chair transition state **E** having the trimethylsilyl group on the equatorial position accounted for the formation of silyl cyclopentanol *cis*-**65**. The samarium ion with coordination of HMPA and other ligands might exert severe eclipsed interaction in the transition state **F**. The dipole−dipole interaction between the oxide and double bond might also disfavor **F**. The preference of **G** over **H** diminished when a bulkier Ph_2MeSi group was used, so that both pathways proceeded to give two diastereomers of **66**. Similar stereochemistry has been reported in the SmI_2-promoted ketyl−olefin radical cyclization reactions.[34e,f] Compound **66** was also derived from the addition of silyl substituted *O*-stannyl ketyl to the olefin. The stereochemical outcome (*cis*/*trans* = 5:1)

Scheme 8

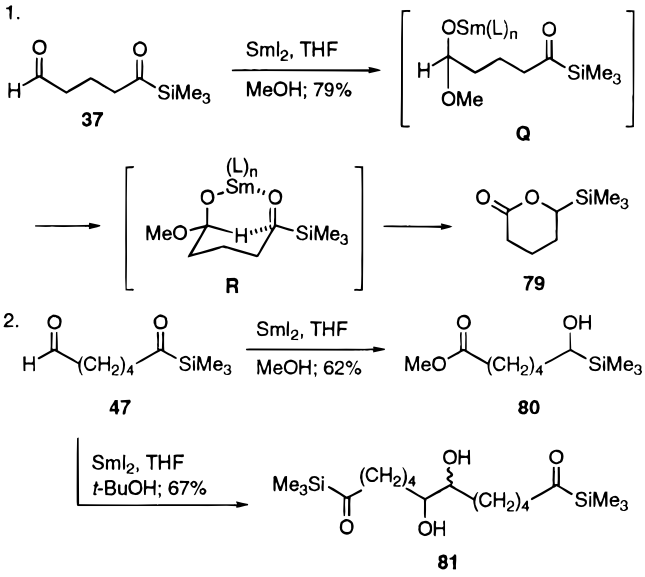


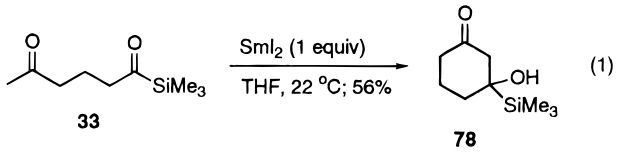
indicated that the chair transition state **I**, in which the *O*-stannyl group occupied the axial position,[34,35] was preferred over **J**. Diol **67** was obtained presumably by addition of **21** with an organosamarium **L**, which was resulted from further reduction of the radical cyclization intermediate **K**.

1,8-Bis(trimethylsilyl)-1,8-octanedione (**31**) was reduced with SmI_2 (Scheme 8) to give 8-hydroxy-1,8-bis-(trimethylsilyl)octanone (**71**, one-site reduction, 53%) and 1,8-bis(trimethylsilyl)-1,8-hexanediol (**74**, two-site reduction, 36%). 1,5-Bis(trimethylsilyl)-1,5-pentanedione (**28**) underwent a one-site reduction with SmI_2 (2 equiv), and the product 5-hydroxy-1,5-bis(trimethylsilyl)pentanone (**69**) further condensed to its dihydropyran form **75**. When bis-acyl silane **29** was treated with tributyltin hydride (2 equiv) in refluxing benzene in the presence of catalytic amount of AIBN, diol **72** was obtained in 12% yield along with 52% of dihydropyran **76**. Apparently, the silyl substituted *O*-stannyl ketyl did not add to the acylsilane intramolecularly. This is in sharp contrast to the related intramolecular 1,5-cyclizations of alkyl substituted carbon radicals to acyl silanes.[17c]

Treatment of 1,6-bis(trimethylsilyl)-1,6-hexanedione (**30**) with SmI_2 (2.5 equiv) afforded mainly an aldol product **77** (46%)[36] in addition to the one-site reduction product **70** (13%) and the two-site reduction product **73** (9%). An NOE study, *i.e.* irradiation of the resonance of Me_3Si group (at δ −0.05) causing a 20% NOE of the resonance of α-proton, established that aldol **77** had the hydroxyl and acyl groups on the same face. In such a case, SmI_2 presumably functioned as a Lewis acid to induce the acyl silane to form an (*E*)-enolate and the subsequent aldol reaction proceeded with a chelate mode **P**.[37]

Scheme 9





1-(Trimethylsilyl)-1,5-hexanedione (**33**) reacted with SmI_2 (eq 1) to give an aldol product **78** (56%) but no reduction product. No reaction of **33** occurred in the presence of a proton source (MeOH or *t*-BuOH), and the starting material was recovered. On the other hand, 1-(trimethylsilyl)-1,5-pentanedione (**37**) reacted with SmI_2 (Scheme 9) in the presence of MeOH to give a *δ*-silyl-*δ*-lactone **79** (79%). The reaction was presumably initiated by addition of MeOH to the aldehyde group to form a hemiacetal with catalysis of SmI_2. The intermediate **Q** underwent Tishchenko reaction[36,38] by hydride transfer to the acyl silane **R** and led to the observed lactone **79**. 1-(Trimethylsilyl)-1,6-hexanedione (**47**) reacted similarly with SmI_2 (Scheme 9) in THF/MeOH to give a methyl ester **80** (62%). The reaction in THF/*t*-BuOH gave, however, pinacols **81** resulted from reductive coupling of the formyl groups.[36,39]

When 1-(dimethylphenylsilyl)-1,5-pentanedione (**46**) was treated with 1.5 equiv of tributyltin hydride (Scheme 10), cyclization did occur to give monosilylated 1,2-cyclopentanediol *cis*-**82** (21%) and *trans*-**82** (18%), and *cis*-diol **83** (32%). Diol **83** was resulted from desilylation of *cis*-**82** during silica gel column chromatographic purification. The stereochemistry of **82** was determined by comparison with the authentic samples prepared by silylation of the commercially available diols. The reaction of 1-(dimethylphenylsilyl)-1,7-heptanedione (**48**) with tributyltin hydride (1 equiv) gave only silyl alcohol **84** in

(34) For general radical cyclizations, see: (a) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073. (b) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925. (c) Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 959. For *O*-stannyl ketyl related cyclizations, see: (d) Hon, Y.-S.; Sun, P.-P.; Lu, H.-L.; Chang, N.-C. *J. Chin. Chem. Soc.* **1994**, *41*, 445. For *O*-samarium ketyl related cyclizations, see: (e) Molander, G. A.; Mckie, J. A. *J. Org. Chem.* **1992**, *57*, 3132. (f) Molander, G. A.; Kenny, C. *J. Am. Chem. Soc.* **1989**, *111*, 8236. (g) Molander, G. A.; Mckie, J. A. *J. Org. Chem.* **1995**, *60*, 872.

(35) Enholm, E. J.; Prasad, G. *Tetrahedron Lett.* **1989**, *30*, 4939.

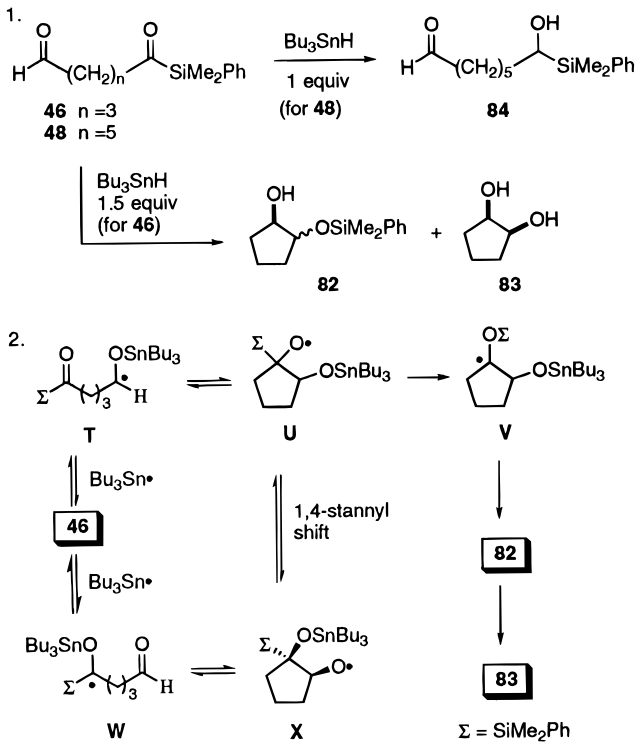
(36) Some aldol products have been observed in the SmI_2(*Ot*-Bu) promoted reaction of 5-oxohexanal, see: Unenishi, J.; Masuda, S.; Wakabayashi, S. *Tetrahedron Lett.* **1991**, *32*, 5097.

(37) Heathcock, C. H. in *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, Chap. 1.5.

(38) Evans, D. A.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1990**, *112*, 6447 and the references cited therein.

(39) Namy, J. L.; Souppe, J.; Kagan, H. B. *Tetrahedron Lett.* **1983**, *24*, 765.

Scheme 10



38% yield along with unreacted starting material. It is noted that no cyclization of this type was observed in the related system of **37** when SmI_2 was used.

Mechanistically, there are two possible pathways to account for the formation of **82**. Stannyl radical addition to the formyl group would give *O*-stannyl ketyl **S** which could cyclize onto the acyl silane group to give the β-silyl alkoxy radical **T**. Radical Brook rearrangement of **T** led to the formation of **U**.[17] Alternatively, the stannyl radical could also add to the acyl silane group to give the ketyl **V**. Addition of this radical to the formyl group would give alkoxy radical **W**. In principle, a 1,4-stannyl shift might occur to give **T**.[22g,40] Currently, we have no evidence to determine which pathway is preferred; however, the preferential reduction of the acyl silane moiety in **48** is worth noting. The stereochemical outcome was determined at the stage of hydrogen abstraction of radical **U**. The moderate *cis*-selectivity, (*cis*-**82** + **83**)/*trans*-**82** = 3:1, was likely due to the approaching of tributyltin hydride opposite to the stannyloxy group.[41] The decreased *cis*-selectivity (1.5:1) in the formation of **67** (Scheme 6) was possibly due to the presence of a bulkier (tributylstannyl)-methyl group which might destabilize *cis*-**67**. Compared with the case of **29** (Scheme 8), we attributed the lack of radical cyclization reactivity of **29** to the steric effect between the two bulky silyl groups. Removal of one of the silyl groups facilitated the cyclization.

Conclusion

Acyl silanes were generally reduced with SmI_2 in THF to give the corresponding α-silyl alcohols without transfer of silyl groups (via Brook rearrangements). Bromophenyl or succinimide substituents were inert to SmI_2 under the reaction conditions. The presumed organosamarium species such as that depicted in **B** (Scheme 5) were successfully alkylated intra- or intermolecularly to give α-silyl cycloalkanols or tertiary α-silyl alcohols. The reaction of benzoyl trimethylsilane with SmI_2 in the presence of HMPA also afforded a side product, benzyl phenyl ketone, presumably derived from the picanol coupling reaction followed by sequential transfers of the silyl groups.

Intramolecular radical cyclizations of 5-hexenoyl silanes were effected with SmI_2 or Bu_3SnH to give α-silyl cyclopentanols. The radical cyclizations proceeded with similar mechanisms via the chairlike transition states, though SmI_2 appeared to be a better reagent than Bu_3SnH in these reactions. The radical cyclizations favored to give the products having the *cis*-configuration, though the stereoselectivity depended on the reagents and the bulkiness of silyl groups. Treatment of 1-silyl-1,5-pentanedione with Bu_3SnH (Scheme 10) also yielded intramolecular cycliaztion products. Treatments of bis-acyl silanes with SmI_2 or Bu_3SnH generally gave reduction products (one- or two-site reduction). No radical cyclization product was formed presumably due to the steric effect between the two bulky silyl groups.

The pinacol coupling reaction of 1-(trimethylsilyl)-1,6-hexanedione was carried out with SmI_2 in the presence of *t*-BuOH (Scheme 9). On the other hand, a Tishchenko reaction occurred to give methyl 6-hydroxy-6-(trimethylsilyl)hexanoate when the reaction was conducted in the presence of MeOH. The reaction of 1-silyl-1,5-pentanedione with SmI_2 in the presence of MeOH proceeded similarly to give a δ-silyl-δ-lactone.

Unprecedent intramolecular aldol reactions of 1-(trimethylsilyl)-1,5-hexanedione was observed on treating with SmI_2 (eq 1). Under the similar reaction conditions, an aldol reaction of 1,5-bis(trimethylsilyl)-1,6-hexanedione (Scheme 8) occurred by forming an (*E*)-enolate from one of the acyl silane group and added intramolecularly to the other acyl silane via a chelate transition state.

In summary, we have prepared a series of acyl silanes including aliphatic-, aromatic-, and bis-acyl silanes, as well as the acyl silanes bearing other substituents such as bromine atom, alkenyl, succinimide and carbonyl groups. The reactions of acyl silanes with SmI_2 or Bu_3SnH occurring in various manners such as reductions, reductive alkylations, intramolecular radical cyclizations, pinacol couplings, aldol reactions, and Tishchenko reactions were of synthetic interest.

Experimental Section

Melting points are uncorrected. ^1H NMR spectra were recorded at 200, 300, or 400 MHz; ^{13}C NMR spectra were recorded at 50, 75, or 100 MHz. Tetramethylsilane (δ = 0 ppm) was used as internal standard in ^1H NMR spectra. Mass spectra were recorded at an ionizing voltage of 70 eV or 20 eV. Merck silica gel 60F sheets were used for analytical thin-layer chromatography. Column chromatography was performed on SiO_2 (70−230 mesh); gradients of EtOAc and *n*-hexane were used as eluents. High-pressure liquid chromatography was carried out on a liquid chromatograph equipped with a refractive index detector. The samples were analyzed and/or separated on a Hibar Lichrosorb Si 60 (7 μm) column (25 cm × 1 cm) with the indicated eluent with a 5 mL/min flow rate. Benzene and THF were distilled from sodium benzophenone ketyl under N_2.

General Procedure for the Preparation of 2-(Trialkylsilyl)-1,3-dithianes. To a cold (0 °C) stirred solution of 1,3-dithiane (2 g, 16.7 mmol) in THF (16 mL) was added dropwise BuLi (15.1 mL of 1.6 M solution in hexane, 22.5 mmol). The mixture was stirred for 10 min, and then trialkylsilyl chloride (16.7 mmol) was added in one portion. The resulting solution

(40) (a) Davies, A. G.; Tse, M.-W. *J. Organomet. Chem.* **1978**, *155*, 25. (b) Hasegawa, E.; Ishiyama, K.; Kato, T.; Horaguchi, T.; Shimizu, T. *J. Org. Chem.* **1992**, *57*, 5352.

(41) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969.

was stirred for another 30 min and then slowly warmed to room temperature (32 °C). The reaction was quenched by addition of aqueous NH_4Cl. The mixture was concentrated, and the residue was taken up in EtOAc (50 mL). The organic phase was washed with brine (2 × 25 mL), dried (Na_2SO_4), and concentrated on rotary evaporation to give a crude product of 2-(trialkylsilyl)-1,3-dithiane. Separation of the product was accomplished by silica gel chromatography using EtOAc/hexane as eluent.

General Procedure for the Preparation of 2-Alkyl-2-(trialkylsilyl)-1,3-dithianes. To a cold (0 °C) stirred solution of 2-(trialkylsilyl)-1,3-dithiane (5−10 mmol, 1 equiv) in THF (30 mL) was added dropwise BuLi (1.2 equiv of 1.6 M solution in hexane). The mixture was stirred for 10 min, and an alkylating agent (1.2 equiv) was added in one portion. The resulting solution was stirred for another 30 min and then slowly warmed to room temperature (32 °C). The reaction was quenched by addition of aqueous NH_4Cl. The mixture was concentrated, and the residue was taken up in EtOAc (30 mL). The organic phase was washed with brine (2 × 15 mL), dried (Na_2SO_4), and concentrated on rotary evaporation to give a crude product of 2-alkyl-2-(trialkylsilyl)-1,3-dithiane. Separation of the product was accomplished by silica gel chromatography using EtOAc/hexane as eluent.

General Procedure for the Preparation of Acyl Silanes. Method A. To a mixture of $BF_3{\cdot}OEt_2$ (0.73 mL, 6 mmol), Celite (1 g), and HgO (1.3 g, 6 mmol) in 10 mL of THF/H_2O (v/v = 85:15) was added 2-alkyl-2-(trialkylsilyl)-1,3-dithiane in THF (6 mL) dropwise at room temperature (28 °C). The mixture was stirred for 1 h at room temperature (28 °C), after which the mixture was filtered through a short column containing silica gel and Celite. The solution was diluted with ether (30 mL), washed with brine (2 × 15 mL), dried (Na_2SO_4), and concentrated on rotary evaporation to give a crude product of acyl silane. Separation of the product was accomplished by silica gel chromatography using EtOAc/hexane as eluent.

Method B. To a cold (−30 °C) solution of 2-alkyl-2-(trialkylsilyl)-1,3-dithiane (10 mmol, 1 equiv), Celite (60 mg/mmol), and $NaHCO_3$ (1.5 equiv) in CH_2Cl_2/CH_3CN (v/v = 3:2, 50 mL) was added ammonium cerium(IV) nitrate (CAN, 3 equiv) in CH_3CN/H_2O (v/v = 15:1, 20 mL) over a period of 10 min. The resulting solution was stirred at −30 °C for 5 min and then diluted with 100 mL of ether, filtered, and partitioned with 50 mL of water. The ethereal phase was washed with brine (2 × 20 mL), dried over Na_2SO_4, and filtered, and the filtrate was concentrated on rotary evaporation to give a crude product of acyl silane. Separation of the product was accomplished by silica gel chromatography using EtOAc/hexane as eluent.

Benzoyltrimethylsilane (2).[23b] 2-Phenyl-2-(trimethylsilyl)-1,3-dithiane (**1**) was hydrolyzed with HgO and $HgCl_2$ in aqueous MeOH to give the acyl silane **2** (82%) according to literature.[23]

1-(Trimethylsilyl)hexanone (4).[24] Compound **4** was prepared from hydroboration−oxidation of 1-hexynyltrimethylsilane **3** (77%) according to literature.[24]

***N*-[3-Oxo-3-(trimethylsilyl)propyl]pyrrolidine-2,5-dione (14).** Alkylation of 2-(trimethylsilyl)-1,3-dithiane (5.04 mmol) with 2-chloroethanol tetrahydropyran ether (2.16 g, 6.05 mmol), followed by hydrolysis (cat. TsOH, MeOH, 25 °C, 2 h), gave 2-(2-hydroxyethyl)-2-(trimethylsilyl)-1,3-dithiane[30] (0.83 g, 70%). Solid, mp 46−48 °C. Condensation of the alcohol (0.80 g, 3.4 mmol) with succinimide (0.4 g, 4 mmol) according to Mitsunobu procedure, using PPh_3 (1.6 g, 5.1 mmol) and diethyl azodicarboxylate (0.53 mL, 3.4 mmol) in THF at 0 °C for 12 h, gave 2-[(2-succinimidyl)ethyl]-2-(trimethylsilyl)-1,3-dithiane (**6**, 0.84 g, 77%). Solid, mp 134−136 °C. The dithiane **6** (0.7 g, 2.57 mmol) was treated with CAN to give the title compound **14** (450 mg, 82%). Solid, mp 125−126 °C; TLC (EtOAc/hexane (50:50)) R_f = 0.1; IR (KBr) 2960, 1708, 1630, 1436, 1397, 1250, 1152 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 9 H), 2.66 (s, 4 H), 2.87 (t, J = 7.0 Hz, 2 H), 3.70 (t, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −3.4 (q, 3 C), 28.0 (t, 2 C), 32.9 (t), 44.9 (t), 176.9 (s, 2 C), 245.0 (s); MS m/z (rel intensity) 227 (M^+, 1), 212 (3), 199 (15), 170 (13), 156 (14), 103 (5), 73 (100); HRMS calcd for $C_{10}H_{17}NO_3Si$ 227.0978, found 227.0974.

3-(2-Bromophenyl)-1-(trimethylsilyl)propanone (15). A crude 2-[2-(*o*-bromophenyl)ethyl]-2-(trimethylsilyl)-1,3-dithiane (**7**, 0.92 g, 2.4 mmol), prepared from 1-bromo-2-(2-bromoethyl)-benzene (0.69 g, 2.61 mmol) and 2-(trimethylsilyl)-1,3-dithiane (0.5 g, 2.65 mmol), was treated with HgO (1.06 g, 4.8 mmol) and $BF_3{\cdot}OEt_2$ (0.59 mL, 4.8 mmol) to give the title compound **15** (302 mg, 44%). An oil; TLC (EtOAc/hexane (2:98)) R_f = 0.17; IR (neat) 3061, 2956, 2897, 1635, 1463, 1246, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 9 H), 2.90 (s, 4 H), 6.93−7.02 (m, 1 H), 7.10−7.18 (m, 2 H), 7.45 (d, J = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −3.4 (q, 3 C), 28.7 (t), 47.7 (t), 120.4 (s), 127.3 (d), 127.5 (d), 130.4 (d), 132.6 (d), 140.7 (s), 246.0 (s); MS m/z (rel intensity) 286 (M^+, 10), 271 (17), 269 (16), 243 (13), 241 (12), 205 (29), 73 (100); HRMS calcd for $C_{12}H_{17}BrOSi$ 286.0211, found 286.0227.

3-(2-Bromophenyl)-1-(diphenylmethylsilyl)propanone (16). A crude 2-[2-(*o*-bromophenyl)ethyl]-2-(diphenylmethylsilyl)-1,3-dithiane (**8**, 2.2 g, 4.4 mmol), prepared from 1-bromo-2-(2-bromoethyl)benzene (1.32 g, 5 mmol) and 2-(diphenylmethylsilyl)-1,3-dithiane (1.58 g, 5 mmol), was treated with HgO (1.9 g, 8.8 mmol) and $BF_3{\cdot}OEt_2$ (1.08 mL, 8.8 mmol) to give the title compound **16** (470 mg, 23%). An oil; TLC (EtOAc/hexane (2:98)) R_f = 0.1; IR (neat) 3066, 3018, 2958, 1635, 1462, 1251, 996 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.74 (s, 3 H), 2.95 (m, 4 H), 6.99−7.14 (m, 3 H), 7.33−7.46 (m, 7 H), 7.55 (d, J = 7.8 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ −5.5 (q), 28.8 (t), 48.9 (t), 124.1 (s), 127.3 (d), 127.5 (d), 128.1 (d, 4 C), 130.0 (d, 2 C), 130.4 (d), 132.3 (s, 2 C), 132.6 (d), 138.4 (d, 4 C), 140.4 (s), 242.6 (s); MS m/z (rel intensity) 409 (M^+, 40), 367 (60), 358 (25), 252 (8), 225 (36), 197 (100), 137 (10); HRMS calcd for $C_{22}H_{21}BrOSi$ 410.0524, found 410.0537.

5-Bromo-1-(dimethylphenylsilyl)pentanone (17). A crude 2-(4-bromobutyl)-2-(dimethylphenylsilyl)-1,3-dithiane (**9**, 1.60 g), prepared from 2-(dimethylphenylsilyl)-1,3-dithiane (0.76 g, 3 mmol) and 1,4-dibromobutane (1.2 mL, 9 mmol), was treated with HgO (1.3 g, 6 mmol) and $BF_3{\cdot}OEt_2$ (0.73 mL, 6 mmol) to give the title compound **17** (0.6 g, 67%). An oil; TLC (EtOAc/hexane (2:98)) R_f = 0.14; IR (neat) 2944, 1642, 1428, 1250, 1110, 836, 818 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.47 (s, 6 H), 1.53−1.74 (m, 4 H), 2.57 (t, J = 6.0 Hz, 2 H), 3.27 (t, J = 6.0 Hz, 2 H), 7.35−7.55 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −4.8 (q, 2 C), 20.7 (t), 32.0 (t), 33.2 (t), 47.4 (t), 128.1 (d, 2 C), 129.9 (d), 138.8 (d, 2 C), 154.2 (s), 245.4 (s); MS m/z (rel intensity) 299 (M^+ − 1, 0.5), 297 (0.5), 271 (2), 269 (2), 201 (8), 199 (8), 135 (100); HRMS calcd for $C_{13}H_{19}BrOSi$ 300.0369, found 300.0367.

6-Bromo-1-(*tert*-butyldimethylsilyl)hexanone (18). A crude 2-(5-bromopentyl)-2-(*tert*-butyldimethylsilyl)-1,3-dithiane (**10**, 1.04 g), prepared from 2-(*tert*-butyldimethylsilyl)-1,3-dithiane (0.7 g, 3 mmol) and 1,5-dibromopenane (1.2 mL, 9 mmol), was treated with HgO (1.39 g, 6 mmol) and $BF_3{\cdot}OEt_2$ (0.73 mL, 6 mmol) to give the title compound **18** (0.61 g, 70%). An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.3; IR (neat) 2927, 2854, 1634, 1459, 1248, 837, 775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 6 H), 0.90 (s, 9 H), 1.31−1.59 (m, 4 H), 1.82 (quin, J = 7.2 Hz, 2 H), 2.58 (t, J = 7.0 Hz, 2 H), 3.37 (t, J = 6.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −7.0 (q, 2 C), 16.4 (s), 20.9 (t), 26.3 (q, 3 C), 27.7 (t), 32.6 (t), 33.5 (t), 49.8 (t), 247.0 (s); MS m/z (rel intensity) 294 (M^+ + 1, 2), 237 (6), 213 (9), 195 (26), 171 (8), 115 (82), 73 (100); HRMS calcd for $C_{12}H_{25}BrOSi$ 292.0858, found 292.0855.

7-Bromo-1-(trimethylsilyl)heptanone (19). A crude 2-(6-bromohexyl)-2-(trimethylsilyl)-1,3-dithiane (**11**, 0.97 g), prepared from 2-(trimethylsilyl)-1,3-dithiane (0.58 g, 3 mmol) and 1,6-dibromohexane (1.38 mL, 9 mmol), was treated with HgO (1.39 g, 6 mmol) and $BF_3{\cdot}OEt_2$ (0.73 mL, 6 mmol) to give the title compound **19** (0.52 g, 65%). An oil; TLC (EtOAc/hexane (10:90)) R_f = 0.5; IR (neat) 2934, 2858, 1634, 1457, 1246, 844, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.13 (s, 9 H), 1.16−1.54 (m, 6 H), 1.78 (quin, J = 6.8 Hz, 2 H), 2.54 (t, J = 7.0 Hz, 2 H), 3.33 (t, J = 6.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −3.2 (q, 3 C), 21.7 (t), 27.8 (t), 28.3 (d), 32.4 (t), 33.6 (t), 48.0 (t), 248.0 (s); MS m/z (rel intensity) 251 (M^+ − 15, 1), 249 (1), 185 (2), 139 (6), 101 (6), 95 (15), 73 (100); HRMS calcd for $C_{10}H_{21}BrOSi$ 266.0524, found 266.0527.

1-(Trimethylsilyl)-5-hexenone (20). 2-(4-Pentyl)-2-(trimethylsilyl)-1,3-dithiane (**12**, 1.83 g, 7 mmol), prepared from 2-(trimethylsilyl)-1,3-dithiane (1.92 g, 10 mmol) and 5-bromo-

1-pentene (1.42 mL, 12 mmol), was treated with CAN (11.5 g, 21 mmol) to give the title compound **20** (0.91 g, 76%). An oil; TLC (EtOAc/hexane (2:98)) R_f = 0.3; IR (neat) 2954, 1634, 1436, 1399, 1247, 911, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.12 (s, 9 H), 1.55 (quin, J = 7.2 Hz, 2 H), 1.95 (q, J = 7.2 Hz, 2 H), 2.53 (t, J = 7.2 Hz, 2 H), 4.86−4.96 (m, 2 H), 5.57−5.78 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ −3.3 (q, 3 C), 21.1 (t), 33.1 (t), 47.4 (t), 114.9 (t), 138.1 (d), 247.0 (s); MS m/z (rel intensity) 170 (M^+, 3), 169 (4), 155 (5), 127 (6), 101 (5), 75 (20), 73 (100); HRMS calcd for $C_9H_{18}OSi$ 170.1127, found 170.1126.

1-(Diphenylmethylsilyl)-5-hexenone (21). 2-(4-Pentyl)-2-(diphenylmethylsilyl)-1,3-dithiane (**13**, 2.8 g, 7.3 mmol), prepared from 2-(diphenylmethylsilyl)-1,3-dithiane (2.4 g, 7.5 mmol) and 5-bromo-1-pentene (1.07 mL, 9.12 mmol), was treated with CAN (11.9 g, 21.9 mmol) to give the title compound **21** (1.62 g, 76%). An oil; TLC (EtOAc/hexane (2:98)) R_f = 0.2; IR (neat) 3064, 3044, 2929, 1636, 1424, 1111, 997 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.73 (s, 3 H), 1.56 (quin, J = 7.4 Hz, 2 H), 1.92 (q, J = 7.4 Hz, 2 H), 2.65 (t, J = 7.4 Hz, 2 H), 4.83−4.93 (m, 2 H), 5.55−5.75 (m, 1 H), 7.33−7.43 (m, 6 H), 7.51−7.59 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −5.3, 21.2, 33.0, 48.8, 115.0, 128.2, 130.1, 132.8, 135.0, 138.1, 244.3; MS m/z (rel intensity) 294 (M^+, 8), 293 (41), 197 (100), 137 (20), 84 (20), 49 (51); HRMS calcd for $C_{19}H_{22}OSi$ 294.1442, found 294.1441.

1,5-Bis(trimethylsilyl)-1,5-pentanedione (28). To a cold (0 °C) stirred solution of 2-(trimethylsilyl)-1,3-dithiane (962 mg, 5 mmol) in THF (5 mL) was added dropwise BuLi (3.43 mL of 1.6 M solution in hexane, 5.5 mmol) under Ar. The mixture was stirred at 0 °C for 20 min, and then 1,3-dibromopropane (0.25 mL, 2.5 mmol) was added. The resulting solution was stirred for another 30 min, and quenched by addition of aqueous NH_4Cl. The volatile components were removed by rotary evaporator, and the residue was taken up in EtOAc. The organic phase was washed with brine (2 × 15 mL), dried (Na_2SO_4), and concentrated on rotary evaporation to give a crude product of bis-dithiane **24** (1.26 g). To a mixture of $BF_3{\cdot}OEt_2$ (1.48 mL, 12 mmol), Celite (1 g), and HgO (2.5 g, 12 mmol) in 10 mL of THF/H_2O (v/v = 85:15) was added the crude bis-dithiane **24** in THF (3 mL) dropwise at room temperature. The mixture was stirred for 20 min and filtered through a short column containing silica gel and Celite. The solution was partitioned between ether (20 mL) and water (10 mL), washed with brine (2 × 15 mL), dried (Na_2SO_4), and concentrated on rotary evaporation. The residue was purified by silica gel chromatography with elution of EtOAc/hexane (5:95) to give the title compound **28** (412 mg, 68%). An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.23; IR (neat) 2958, 2901, 1642, 1401, 1249, 844, 753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 18 H), 1.70 (quin, J = 6.8 Hz, 2 H), 2.56 (t, J = 6.8 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ −3.3 (q, 6 C), 14.7 (t), 47.3 (t, 2 C), 247.7 (s, 2 C); MS m/z (rel intensity) 244 (M^+, 20), 188 (1),173 (5), 147 (55), 133 (8), 115 (3), 73 (100); HRMS calcd for $C_{11}H_{24}O_2Si_2$ 244.1315, found 244.1311.

1,5-Bis(diphenylmethylsilyl)-1,5-pentanedione (29). Bis-dithiane **25**, prepared from dithiane **23** (0.44 g, 1.4 mmol) and 1-bromo-3-chloropropane (69 μL, 0.7 mmol), was treated with HgO (0.75 g, 3.5 mmol), Celite (0.65 g), and $BF_3{\cdot}OEt_2$ (0.35 mL, 2.8 mmol), by a procedure similar to that for **28**, to give **29** (172 mg, 50%) as a light yellow liquid. IR (neat) 3065, 1638, 1425, 1395, 1252, 1112, 997, 792, 728, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70 (s, 6 H), 1.67 (quintet, J = 7.0 Hz, 2 H), 2.56 (t, J = 7.0 Hz, 4 H), 7.29−7.66 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ −5.4, 14.8, 48.6, 128.2, 130.1, 132.6, 134.9, 243.8; MS m/z (rel intensity) 492 (M^+, 70), 356 (6), 333 (15), 255 (21), 197 (100), 117 (11); HRMS calcd for $C_{31}H_{32}O_2Si_2$ 492.1942, found 492.1942.

1,6-Bis(trimethylsilyl)-1,6-hexanedione (30). Compound **30** (65% yield) was prepared from bis-dithiane **26** by a procedure similar to that for **28**. An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.28; IR (neat) 2956, 2901, 1641, 1402, 1249, 844, 752 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 18 H), 1.43 (m, 4 H), 2.55 (t, J = 6.8 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ −3.1 (q, 6 C), 21.7 (t, 2 C), 48.2 (t, 2 C), 247.9 (s, 2 C); MS m/z (rel intensity) 258 (M^+, 15), 217 (2), 157 (15), 147 (28), 129 (3), 101 (2), 73 (100); HRMS calcd for $C_{12}H_{26}O_2Si_2$ 258.1471, found 258.1479.

1,8-Bis(trimethylsilyl)-1,8-octanedione (31). Compound **31** (61% yield) was prepared from bis-dithiane **27** by a procedure similar to that for **28**. An oil; TLC (EtOAc/hexane (10:90)) R_f = 0.5; IR (neat) 2934, 1635, 1457, 1398, 1246, 846, 752 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 18 H), 1.16 (quin, J = 6.8 Hz, 4 H), 1.41 (quin, J = 6.8 Hz, 4 H), 2.50 (t, J = 7.2 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ −3.2 (q, 6 C), 21.8 (t, 2 C), 29.0 (t, 2 C), 48.2 (t, 2 C), 248.0 (s, 2 C); MS m/z (rel intensity) 286 (M^+, 3), 243 (3), 217 (6), 204 (3), 185 (9), 147 (27), 73 (100); HRMS calcd for $C_{14}H_{30}O_2Si_2$ 286.1784, found 286.1797.

1-(Trimethylsilyl)-1,5-hexanedione (33). Compound **32** (160 mg, 0.5 mmol), prepared from 2-(trimethylsilyl)-1,3-dithiane (2 g, 10.4 mmol) and 5-chloro-2-pentanone ethylene ketal (1.65 mL, 11 mmol, purchased from Aldrich Co.), was treated with HgO (216.5 mg, 1 mmol) and $BF_3{\cdot}OEt_2$ (0.12 mL, 1 mmol) in THF/H_2O (6.8 mL/1.2 mL) to give the title compound **33** (75 mg, 81%) and its ethylene acetal **34** (15 mg, 13%). When the reaction was performed in Me_2CO/H_2O (6.8 mL/1.2 mL), only **33** (85 mg, 91%) was obtained. **33**: An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.14; IR (neat) 2957, 2900, 1715, 1641, 1366, 1249, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 9 H), 1.76 (quin, J = 7.0 Hz, 2 H), 2.09 (s, 3 H), 2.39 (t, J = 7.0 Hz, 2 H), 2.60 (t, J = 7.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −3.2 (q, 3 C), 16.2 (t), 29.8 (q), 42.7 (t), 47.1 (t), 208.5 (s), 247.6 (s); MS m/z (rel intensity) 186 (M^+, 2), 168 (4), 153 (6), 130 (56), 115 (80), 101 (8), 73 (100); HRMS calcd for $C_9H_{18}O_2Si$ 186.1076, found 186.1094. **34**: An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.1; IR (neat) 2955, 2882, 1716, 1362, 1246, 1105, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9 H), 1.54−1.60 (m, 4 H), 2.10 (s, 3 H), 2.40 (t, J = 6.6 Hz, 2 H), 3.79−3.81 (m, 2 H), 3.91−3.96 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −3.2 (q, 3 C), 17.7 (t), 29.8 (q), 35.9 (t), 43.9 (t), 65.2 (t, 2 C), 109.0 (s), 208.8 (s); MS m/z (rel intensity) 231 (M^+ + 1, 30), 215 (9), 201 (10), 157 (100), 145 (31), 99 (60), 73 (65); HRMS calcd for $C_{10}H_{19}O_3Si$ 215.1103, found 215.1113.

1-(Trimethylsilyl)-1,5-pentanedione (37). A mixture of 2-(trimethylsilyl)-1,3-dithiane (2 equiv) and 4-chlorobutanol (2 equiv) in THF was treated with LDA (3.3 equiv) at −78 °C gave **35** in quantitative yield. To a suspension of **35** (2.64 g, 10 mmol), 4A molecular sieve (5 g), and Celite (2.64 g) in CH_2Cl_2 (40 mL) was added PCC (4.31 g, 20 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched by addition of 30 mL of EtOAc/hexane (9:1) and filtered. The solvent was removed on rotary evaporation and purified by silica gel chromatography with elution of EtOAc/hexane (10:90) to give 4-[1-(trimethylsilyl)-2,6-dithiacyclohexyl]butanal (**36**) (1.17 g, 45%). Aldehyde **36** (262 mg, 1 mmol) was treated with HgO (500 mg, 2.3 mmol) and $BF_3{\cdot}OEt_2$ (0.12 mL, 1 mmol) to give the title compound **37** (133 mg, 77%) and its dihydropyran derivative **38** (26 mg, 15%). **36**: An oil; TLC (EtOAc/hexane (10:90)) R_f = 0.26; IR (neat) 2950, 2850, 1722, 1248, 844 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.18 (s, 9 H), 1.79−2.05 (m, 4 H), 2.39−2.52 (m, 4 H), 3.00 (br t, J = 14.0 Hz, 2 H), 9.78 (t, J = 1.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −2.5 (q, 3 C), 20.3 (t), 23.3 (t, 2 C), 24.9 (t), 36.7 (t), 38.4 (s), 43.9 (t), 201.9 (s). **37**: An oil; TLC (EtOAc/hexane (10:90)) R_f = 0.17; IR (neat) 2956, 1723, 1640, 1407, 1249, 845, 753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 9 H), 1.82 (quin, J = 7.0 Hz, 2 H), 2.41 (t, J = 7.0 Hz, 2 H), 2.64 (t, J = 7.0 Hz, 2 H), 9.70 (t, J = 1.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −3.2 (q, 3 C), 14.5 (t), 43.1 (t), 46.9 (t), 202.0 (d), 247.1 (s); MS m/z (rel intensity) 172 (M^+, 4), 157 (10), 116 (30), 101 (44), 73 (100), 59 (8), 45 (12); HRMS calcd for $C_8H_{16}O_2Si$ 172.0919, found 172.0925. **38**: An oil; TLC (EtOAc/hexane (10:90)) R_f = 0.22; IR (neat) 3400, 2956, 1622, 1407, 1247, 1221, 1041, 842 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.06 (s, 9 H), 1.68−2.17 (m, 4 H), 2.97 (d, J = 4.5 Hz, 1 H), 5.04 (t, J = 3.9 Hz, 1 H), 5.26 (br d, J = 2.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −2.5 (q, 3 C), 17.2 (t), 27.3 (t), 91.6 (d), 110.6 (d), 156.8 (s); MS m/z (rel intensity) 172 (M^+, 5), 157 (7), 116 (20), 101 (35), 73 (100), 59 (7), 45 (7); HRMS calcd for $C_8H_{15}O_2Si$ 171.0841, found 171.0856.

1,3-Bis(2,6-dithiacyclohexyl)propane (39).[28] To a mixture of a 50% aqueous solution of glutaric dialdehyde (2.72 mL, 15 mmol), 1,3-propanedithiol (3.0 mL, 30 mmol), and $CHCl_3$ (40 mL) was added $BF_3{\cdot}OEt_2$ (1.0 mL, 11 mmol) in several portions over 2 days. The resulting mixture was partitioned between ether (100 mL) and water (80 mL). The organic phase was washed with brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on silica gel (EtOAc/hexane (4:96)) to give **39** (2.3 g, 55%) as a

white solid; mp 100−100.5 °C (lit.[28] 101.5−102 °C); IR (CH_2Cl_2) 2937, 2901, 1417, 1183, 1008, 906, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65−2.00 (m, 8 H), 2.00−2.18 (m, 2 H), 2.73−2.97 (m, 8 H), 4.01 (br t, J = 6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 23.7, 25.9, 30.3, 34.7, 47.1.

1,5-Bis(2,6-dithiacyclohexyl)pentane (41). Alkylation of 1,3-dithiane (2.4 g, 20 mmol) with 1,5-dibromopentane (1.36 mL, 10 mmol), by a procedure similar to that reported for **28**, gave **41** (2.34 g, 76%) as a white solid. Mp 56−57 °C; IR (CH_2Cl_2) 2935, 2903, 2856, 1455, 1419, 1410, 1271, 1182, 907, 732, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20−1.33 (quintet, J = 7.0 Hz, 4 H), 1.65−1.75 (q, J = 7.0 Hz, 4 H), 1.75−1.90 (m, 2 H), 2.72−2.90 (m, 8 H), 3.98 (t, J = 7.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.9, 26.2, 28.7, 30.4, 35.2, 47.4. Anal. Calcd for $C_{13}H_{24}S_4$: C, 50.61; H, 7.84. Found: C, 50.64; H, 7.75.

1-(Dimethylphenylsilyl)-1,5-pentanedione (46). To a solution of **39** (1.1 g, 3.9 mmol) in dry THF (5 mL) was added dropwise at 0 °C a hexane solution of BuLi (1.55 M, 3.0 mL). The reaction mixture was stirred at 0 °C for 10 min followed by the addition of dimethylphenylchlorosilane (0.71 mL, 4.3 mmol) in one portion. The resulting mixture was stirred at 0 °C for 10 min and then partitioned between ether (80 mL) and water (50 mL). The organic layer was washed with brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo to give a liquid. The liquid was mixed with red HgO (3.37 g, 15.6 mmol), THF (16 mL), and water (2 mL), followed by the addition of $BF_3{\cdot}OEt_2$ (1.2 mL, 10 mmol) in one portion. The resulting mixture was stirred at room temperature for 20 min, diluted with ether (50 mL), and filtered through a short pad of silica gel. The filtrate was washed with water (30 mL), brine (30 mL), dried ($MgSO_4$), and concentrated in vacuo to give a liquid. The liquid was chromatographed on silica gel (EtOAc/hexane (2:8) with the addition of a few drops of Et_3N) to afford **46** (0.64 g, 70%) as a light yellow liquid. IR (neat) 2956, 1717, 1633, 1423, 1247, 1110, 836, 779, 735, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.47 (s, 6 H), 1.76 (quintet, J = 7.0 Hz, 2 H), 2.31 (td, J = 7.0, 1.4 Hz, 2 H), 2.60 (t, J = 7.0 Hz, 2 H), 7.25−7.40 (m, 3 H), 7.45−7.60 (m, 2 H), 9.62 (t, J = 1.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −5.0, 14.5, 42.9, 47.2, 128.2, 129.9, 133.9, 134.0, 201.9, 245.2; MS m/z (rel intensity) 234 (M^+, 8), 193 (91), 178 (13), 163 (21), 152(15), 135 (100), 105 (18), 89 (13); HRMS calcd for $C_{13}H_{18}O_2Si$ 234.1076, found 234.1079.

1-(Trimethylsilyl)-1,6-hexanedione (47). Method A. Dithiane **45** (320 mg, 1 mmol), prepared from alkylation of 2-(trimethylsilyl)-1,3-dithiane with 5-bromopentanal ethylene acetal,[29] was stirred with TsOH (22 mg, 0.12 mmol) in acetone (5 mL) at 25 °C for 24 h. The mixture was partitioned between Et_2O (20 mL) and H_2O (10 mL). The organic layer was washed with brine (15 mL × 2), dried (Na_2SO_4), and concentrated. The residue was then treated with HgO (360 mg, 1.66 mmol) and $BF_3{\cdot}OEt_2$ (0.2 mL, 1.66 mmol) according to the general procedure to give **47** (111 mg, 60%).

Method B. The crude 2-(4-bromobutyl)-2-(trimethylsilyl)-1,3-dithiane (**40**), prepared from alkylation of 2-(trimethylsilyl)-1,3-dithiane (2 g, 10.39 mmol) with 1,4-dibromobutane (1.24 mL, 10.5 mmol), was dissolved in THF (15 mL) and added to a solution of 2-lithio-1,3-dithiane (10.8 mmol) in THF (15 mL) at −20 °C under Ar. The reaction was stirred at 0 °C for 20 min and quenched by addition of aqueous NH_4Cl. The organic layer was taken up in EtOAc (60 mL) and washed with H_2O (30 mL × 2), brine (30 mL × 2), dried (Na_2SO_4), and concentrated. The residue was treated with HgO (8.26 g, 38.1 mmol) and $BF_3{\cdot}OEt_2$ (4.69 mL, 38.1 mmol) according to the general procedure to give **47** (520 mg, 27%).

45: An oil; TLC (EtOAc/hexane (10:90)) R_f = 0.24; IR (neat) 2944, 1246, 1138, 1036, 944, 910, 842 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 9 H), 1.44−2.20 (m, 10 H), 2.39 (dt, J = 14.4, 4.2 Hz, 2 H), 2.98 (br t, J = 14.4 Hz, 2 H), 3.80−3.94 (m, 4 H), 4.84 (t, J = 4.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −2.5 (q, 3 C), 23.3 (t, 2 C), 24.5 (t), 25.1 (t), 27.5 (t), 33.7 (t), 37.1 (t), 38.6 (s), 64.8 (t, 2 C), 104.5 (d); MS m/z (rel intensity) 320 (M^+, 6), 247 (11), 215 (8), 185 (4), 153 (16), 139 (12), 73 (100); HRMS calcd for $C_{14}H_{28}O_2S_2Si$ 320.1300, found 320.13026. **47**: An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.11; IR (neat) 2952, 2872, 1722, 1640, 1249, 845, 753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 9 H), 1.49−1.57 (m, 4 H), 2.39 (td, J = 6.8, 1.8 Hz, 2 H), 2.59 (t, J = 6.8 Hz, 2 H), 9.71 (t, J = 1.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −3.2 (q, 3 C), 21.4 (t), 21.7 (t), 43.7 (t), 47.8 (t), 202.2 (d), 247.5 (s); MS m/z (rel intensity) 186 (M^+, 2), 171 (6), 144 (5), 129 (8), 101 (6), 73 (100), 45 (25); HRMS calcd for $C_9H_{18}O_2Si$ 186.1077, found 186.1073.

1-(Dimethylphenylsilyl)-1,7-heptanedione (48). To a solution of **41** (2.25 g, 7.3 mmol) in dry THF (8 mL) was added dropwise at 0 °C a hexane solution of BuLi (1.55 M, 5.2 mL). The resulting solution was stirred at 0 °C for 10 min followed by the addition of dimethylphenylchlorosilane (1.34 mL, 8.03 mmol) in one portion. After stirring for another 10 min at 0 °C, the reaction mixture was partitioned between ether (100 mL) and water (80 mL). The organic layer was washed with brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was mixed with red HgO (6.3 g, 29.2 mmol), THF (30 mL), and water (6 mL), followed by the addition of $BF_3{\cdot}OEt_2$ (2.69 mL, 22.0 mmol) in one portion. The resulting mixture was stirred at room temperature for 0.5 h, diluted with ether (100 mL), and filtered. The filtrate was washed with water (50 mL), brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on silica gel (EtOAc/hexane (1:9)) to give **48** (1.04 g, 55%) as a light yellow liquid: IR (neat) 2934, 1717, 1633, 1423, 1247, 1168, 835, 780, 736, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.46 (s, 6 H), 1.10−1.25 (m, 2 H), 1.35−1.60 (m, 4 H), 2.31 (td, J = 7.0, 2.0 Hz, 2 H), 2.54 (t, J = 7.0 Hz, 2 H), 7.25−7.45 (m, 3 H), 7.45−7.60 (m, 2 H), 9.67 (t, J = 2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −4.9, 21.7, 28.5, 43.5, 48.2, 128.1, 129.8, 133.8, 134.4, 202.4, 246.0; MS m/z (rel intensity) 262 (M^+, 100), 247 (30), 209 (31), 191 (16), 185 (33), 163 (20), 115 (100), 105 (9), 75 (19), 55 (15); HRMS calcd for $C_{15}H_{22}O_2Si$ 262.1389, found 262.1382.

General Procedure for Reactions of Acyl Silanes with Samarium(II) Iodide. Samarium metal (0.33 g, 2.1 mmol) was added under a flow of Ar to an oven-dried round-bottomed flask containing a magnetic stirring bar. The flask and samarium were gently flame-dried and cooled under Ar. THF (20 mL) was added followed by 1,2-diiodoethane (0.5 g, 2 mmol), and the mixture was allowed to stir at room temerature for 2 h. HMPA (0.35 mL, 2 mmol) was added in appropriate cases, and the resulting purple solution was allowed to stir for 30 min. Acyl silane (1 mmol) in THF (20 mL) was added over a period of 10 min. A proton source (MeOH or *t*-BuOH, 2 mmol) or alkylating agent (allyl bromide or benzyl bromide, 1.6 mmol) was added in appropriate cases. After complete addition, the mixture was stirred for 15 min, quenched with H_2O (2 drops), and filtered. The solvent was removed on rotary evaporation. The residue was passed through a short silica gel column to remove HMPA, and products were separated by silica gel chromatography using EtOAc/hexane as eluent.

General Procedure for Reactions of Acyl Silanes with Tributyltin Hydride. To a solution of acyl silane (1.68 mmol) in deoxygenated benzene (17 mL) was added dropwise at 80 °C over 1 h a solution of Bu_3SnH (0.68 mL, 2.52 mmol) and a catalytic amount of AIBN in deoxygenated benzene (17 mL). The resulting solution was stirred at 80 °C for another 1 h and concentrated in vacuo to give an oil. The oil was mixed with a few drops of Et_3N and chromatographed on silica gel to afford products.

α-(Trimethylsilyl)benzyl alcohol (49)[42] and α-Phenylacetophenone (52).[43] The reaction of phenyl trimethylsilyl ketone **2** (178 mg, 1 mmol) with SmI_2 in THF at 28 °C for 1 h gave **49** (113 mg, 63%). The reaction in the presence of HMPA (0.35 mL, 2 mmol) gave **49** (92 mg, 47%) and α-phenylacetophenone (**52**, 54 mg, 30%). Compound **49**-*d* was obtained from the reaction of **2** with SmI_2 in THF/HMPA/*t*-BuOD (2 equiv). **49**: An oil; TLC (EtOAc/hexane (2:98)) R_f = 0.2; IR (neat) 3430, 3061, 2957, 1679, 1445, 1245, 997 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 4.49 (s, 1 H), 7.15−7.28 (m, 5 H); MS m/z (rel intensity) 180 (M^+, 55), 165 (65), 137 (28), 122 (20), 105 (15), 90 (12), 73 (100). **49**-*d*: ^{13}C NMR ($CDCl_3$) δ 69.9 (J_{C-D} = 20.0 Hz). MS m/z (rel intensity) 181 (M^+, 16). **52**: Solid, mp 55−56 °C (lit.[43] mp 55−56 °C).

1-Phenyl-1-(trimethylsilyl)-3-butenol (50). The reaction of phenyl trimethylsilyl ketone **2** (178 mg, 1 mmol) with SmI_2 in THF/HMPA at 25 °C for 15 min, followed by alkylation with

(42) Wright, A.; West, R. *J. Am. Chem. Soc.* **1974**, *96*, 3220
(43) A commercially available compound. *Beil.* 7 (2), 368.

allyl bromide (0.09 mL, 1 mmol) for 2 h, gave **50** (184 mg, 84%). An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.3; IR (neat) 3512, 2951, 1592, 1486, 1437, 1244, 1033 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.03 (s, 9 H), 1.84 (s, 1 H), 2.49 (dd, J = 13.0, 9.4 Hz, 1 H), 2.00 (dd, J = 13.0, 4.6 Hz, 1 H), 5.08−5.18 (m, 2 H), 5.37−5.51 (m, 1 H), 7.09−7.29 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −4.1 (q, 3 C), 41.2 (t), 70.4 (s), 124.9 (d, 2 C), 125.1 (d), 127.9 (d, 2 C), 132.7 (d), 145.6 (s); MS m/z (rel intensity) 220 (M^+, 25), 219 (100), 205 (25), 177 (10), 129 (80), 105 (45), 73 (50); HRMS calcd for $C_{13}H_{20}OSi$ 219.1205, found 219.1195.

1,2-Diphenyl-1-(trimethylsilyl)ethanol (51). The reaction of phenyl trimethylsilyl ketone **2** (90 mg, 0.5 mmol) with SmI_2 in THF/HMPA at 25 °C for 15 min, followed by alkylation with benzyl bromide (0.1 mL, 0.8 mmol) for 2 h, gave **51** (123 mg, 91%). An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.15; IR (neat) 3526, 3062, 2954, 1590, 1486, 1241, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04 (s, 9 H), 1.53 (s, 1 H), 3.16 (d, J = 13.6 Hz, 1 H), 3.50 (d, J=13.6 Hz, 1 H), 6.91−7.30 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ −4.0 (q, 3 C), 42.6 (t), 71.7 (s), 124.9 (d, 2 C), 125.0 (d), 126.5 (d), 127.7 (d, 2 C), 128.0 (d, 2 C), 130.5 (d, 2 C), 135.5 (s), 145.5 (s); MS m/z (rel intensity) 270 (M^+, 45), 253 (5), 179 (48), 165 (24), 105 (100), 91 (14), 73 (22); HRMS calcd for $C_{17}H_{22}OSi$ 270.1440, found 270.1444.

1-(Trimethylsilyl)hexanol (53).[6] The reaction of 1-(trimethylsilyl)-1-hexanone (**4**) (172 mg, 1 mmol) with SmI_2 in THF at 28 °C for 1 h gave **53** (87 mg, 50%). An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.2; ^1H NMR (200 MHz, $CDCl_3$) δ 0.01 (s, 9 H), 0.87 (t, J = 6.6 Hz, 3 H), 1.23−1.33 (m, 6 H), 1.46−1.51 (m, 2 H), 3.27 (t, J = 6.0 Hz, 1 H).

***N*-[3-Hydroxyl-3-(trimethylsilyl)propyl]pyrrolidine-2,5-dione (54).** The reaction of *N*-[3-oxo-3-(trimethylsilyl)-propyl]pyrroline-2,5-dione (**14**) (113 mg, 0.5 mmol) with SmI_2 in THF at 28 °C for 1 h gave **54** (57 mg, 50%). Solid, mp 78−79 °C; TLC (EtOAc/hexane (70:30)) R_f = 0.15; IR (KBr) 3430, 2980, 1750, 1700, 1450, 1240, 880 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.22 (s, 9 H), 1.58−1.70 (m, 2 H), 2.72 (s, 4 H), 2.94−3.02 (m, 2 H), 3.66−3.73 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.1 (q, 3 C), 28.1 (t, 2 C), 31.1 (t), 35.6 (t), 60.7 (d), 178.0 (s, 2 C); MS m/z (rel intensity) 230 (M^+ + 1, 2), 214 (100), 199 (4), 185 (10), 156 (25), 113 (28), 73 (30); HRMS calcd for $C_9H_{16}NO_3Si$ 214.0899, found 214.0907.

3-(2-Bromophenyl)-1-(trimethylsilyl)propanol (55). The reaction of 3-(2-bromophenyl)-1-(trimethylsilyl)propanone **15** (110 mg, 0.38 mmol) with SmI_2 in THF/HMPA/MeOH at 18 °C for 1 h gave **55** (70 mg, 63%). An oil; TLC (EtOAc/hexane (10:90)) R_f = 0.25; IR (neat) 3418, 3058, 1694, 1587, 1560, 1463, 1245 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.03 (s, 9 H), 1.25 (br s, 1 H), 1.75−1.85 (m, 2 H), 2.72−2.80 (m, 1 H), 2.97−3.02 (m, 1 H), 3.31 (dd, J = 9.3, 4.0 Hz, 1 H), 7.01−7.06 (m, 1 H), 7.21−7.23 (m, 2 H), 7.50 (d, J = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −3.9 (q, 3 C), 33.5 (t), 33.7 (t), 65.4 (d), 124.0 (s), 127.4 (d), 127.5 (d), 130.4 (d), 132.7 (d), 141.4 (s); MS m/z (rel intensity) 287 (M^+ − 1, 3), 285 (2), 226 (2), 224 (3), 198 (6), 196 (7), 73 (100); HRMS calcd for $C_{12}H_{18}BrOSi$ 287.0289, found 287.0303.

3-(2-Bromophenyl)-1-(diphenylmethylsilyl)propanol (56). The reaction of 3-(2-bromophenyl)-1-(diphenylmethylsilyl)propanone (**16**) (146 mg, 0.356 mmol) with SmI_2 in THF/HMPA at 28 °C for 1 h gave **56** (75 mg, 52%). An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.25; IR (neat) 3442, 3066, 2922, 1422, 1249, 1110, 789 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.60 (s, 3 H), 1.86−1.98 (m, 2 H), 2.77−2.84 (m, 1 H), 2.99−3.05 (m, 1 H), 3.89−3.93 (m, 1 H), 7.00−7.62 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ −6.7 (q), 33.6 (t, 2 C), 63.9 (d), 124.5 (s), 127.4 (d), 127.5 (d), 128.0 (d, 4 C), 129.6 (d, 2 C), 130.5 (d), 132.7 (d), 134.5 (s, 2 C), 134.9 (d, 2 C), 135.0 (d, 2 C), 141.2 (s); FAB-MS m/z (rel intensity) 412 (M^+, 1), 395 (3), 333 (7), 273 (8), 257 (2), 197 (100), 195 (5); HRMS calcd for $C_{21}H_{20}BrOSi$ 397.0446, found 397.0422.

1-(Dimethylphenylsilyl)cyclopentanol (57). The reaction of 5-bromo-1-(dimethylphenylsilyl)pentanone (**17**) (180 mg, 0.6 mmol) with SmI_2 in THF at 18 °C for 1 h gave **57** (62 mg, 47%). An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.15; IR (neat) 3422, 2958, 2906, 2853, 1427, 1251, 1111 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.33 (s, 6 H), 1.50−1.82 (m, 9 H), 7.32−7.36 (m, 3 H), 7.55−7.59 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −5.6 (q, 2 C), 23.7 (t, 2 C), 37.6 (t, 2 C), 75.0 (s), 127.8 (d, 2 C), 129.2 (d), 134.3 (d, 2 C), 136.8 (s); MS m/z (rel intensity) 219 (M^+ − 1, 1), 205 (25), 187 (6), 135 (100), 121 (9), 75 (60), 58 (9); HRMS calcd for $C_{13}H_{20}OSi$ 220.1283, found 220.1268.

1-(*tert*-Butyldimethylsilyl)cyclohexanol (58) and 6-Bromo-1-(*tert*-butyldimethylsilyl)hexanol (59). The reaction of 6-bromo-1-(*tert*-butyldimethylsilyl)hexanone (**18**) (140 mg, 0.47 mmol) with SmI_2 in THF at 26 °C for 1 h gave **58** (45 mg, 45%) and **59** (24 mg, 17%). **58**: An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.28; IR (neat) 3492, 2929, 2854, 1243, 1127, 1005, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.04 (s, 6 H), 0.94 (s, 9 H), 1.01 (br s, 1 H), 1.42−1.78 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ −8.0 (q, 2 C), 17.9 (s), 19.9 (t, 2 C), 26.0 (t), 27.9 (q, 3 C), 34.1 (t, 2 C), 67.3 (s); MS m/z (rel intensity) 213 (M^+ − 1, 5), 185 (15), 149 (22), 129 (36), 111 (51), 97 (65), 57 (100); HRMS calcd for $C_{12}H_{26}OSi$ 214.1753, found 214.1747. **59**: An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.14; ^1H NMR ($CDCl_3$) δ −0.08 (s, 3 H), −0.01 (s, 3 H), 0.91 (s, 9 H), 1.35−1.87 (m, 8 H), 3.38 (t, J = 6.8 Hz, 2 H), 3.70 (t, J = 6.0 Hz, 1 H); MS m/z (rel intensity) 215 (M^+ − Br, 1), 180 (1), 139 (4), 115 (8), 99 (3), 73 (100), 55 (72); HRMS calcd for $C_{12}H_{26}BrOSi$ 295.0915, found 295.0924.

7-Bromo-1-(trimethylsilyl)heptanol (60). The reaction of 7-bromo-1-(trimethylsilyl)heptanone (**19**) (110 mg, 0.41 mmol) with SmI_2 in THF at 28 °C for 12 h gave **60** (60 mg, 55%). An oil; TLC (EtOAc/hexane (10:90)) R_f = 0.33; IR (neat) 3409, 2926, 2853, 1457, 1244, 839, 749 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 1.10−1.55 (m, 9 H), 1.82 (q, J = 6.8 Hz, 2 H), 3.25 (t, J = 6.8 Hz, 2 H), 3.37 (t, J = 6.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −3.9 (q, 3 C), 26.5 (t), 28.0 (t), 28.6 (t), 32 (t), 33.3 (t), 33.8 (t), 65.9 (d); MS m/z (rel intensity) 267 (M^+, 12), 229 (2), 183 (1), 133 (15), 117 (50), 95 (25), 73 (100); HRMS calcd for $C_{10}H_{22}BrOSi$ 267.0603, found 267.0607.

1-(Trimethylsilyl)-5-hexenol (61) and 1-(Trimethylsilyl)-2-methylcyclopentanol (65). The reaction of 1-(trimethylsilyl)-5-hexenone (**20**) (70 mg, 0.4 mmol) with SmI_2 in THF/*t*-BuOH (0.8 mmol)/HMPA (2 mmol) at 28 °C gave **61** (22 mg, 32%) and **65** (18 mg, 26%). **61**: An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.2; IR (neat) 3402, 3077, 2953, 1632, 1436, 1245, 992 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.02 (s, 9 H), 1.36−1.70 (m, 4 H), 2.01−2.10 (m, 2 H), 3.28 (t, J = 6.8 Hz, 1 H), 4.90−5.05 (m, 2 H), 5.70−5.90 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ −3.9 (q, 3 C), 26.0 (t), 32.9 (t), 33.6 (t), 65.9 (d), 114.5 (t), 138.8 (d); MS m/z (rel intensity) 172 (M^+, 2), 157 (3), 141 (2), 129 (5), 98 (68), 73 (95), 67 (100); HRMS calcd for $C_9H_{20}OSi$ 172.1283, found 172.1283. **65**: An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.25; IR (neat) 3450, 2962, 1457, 1371, 1245, 1205, 930 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (s, 9 H), 0.87 (d, J = 6.8 Hz, 3 H), 1.10−2.05 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ −2.4 (q, 3 C), 18.9 (q), 21.4 (t), 32.2 (t), 35.2 (t), 46.2 (d); ^{13}C NMR (acetone-d_6) δ −2.0 (q, 3 C), 19.1 (q), 22.0 (t), 32.9 (t), 35.5 (t), 46.8 (d), 77.9 (s); MS m/z (rel intensity) 172 (M^+, 1), 155 (8), 127 (6), 113 (2), 98 (10), 90 (26), 67 (100); HRMS calcd for $C_9H_{19}OSi$ 171.1205, found 171.1185.

1-(Diphenylmethylsilyl)-5-hexenol (62) and 1-(Diphenylmethylsilyl)-2-methylcyclopentanol (66). The reaction of 1-(diphenylmethylsilyl)-5-hexenone (**21**) (100 mg, 0.34 mmol) with SmI_2 in THF/HMPA (2 mmol) for 1 h gave **62** (14 mg, 20%), *trans*-**66** (20 mg, 28%), and *cis*-**66** (20 mg, 28%). Compound **62**-*d* was obtained from the reaction of **21** with SmI_2 in THF/HMPA/*t*-BuOD (3 equiv). **62**: An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.15; IR (neat) 3445, 3070, 2929, 1634, 1250, 1188, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.60 (s, 3H), 1.13−2.09 (m, 7 H), 3.89 (t, J = 6.8 Hz, 1 H), 4.89−5.00 (m, 2 H), 5.66−5.87 (m, 1 H) 7.31−7.44 (m, 6 H), 7.56−7.64 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −6.7 (q), 26.1 (t), 32.8 (t), 33.4 (t), 64.4 (d), 114.5 (t), 127.9 (d, 4 C), 129.5 (d, 2 C), 134.9 (d, 2 C), 135.0 (d, 4 C), 138.7 (d); MS m/z (rel intensity) 296 (M^+, 2), 281 (36), 199 (100), 197 (95), 158 (6), 137 (46), 67 (12); HRMS calcd for $C_{19}H_{24}OSi$ 296.1596, found 296.1589. **62**-*d*: ^{13}C NMR ($CDCl_3$) δ 63.8 (J_{C-D} = 20.0 Hz). MS m/z (rel intensity) 297 (M^+, 4). *trans*-**66**: An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.2; HPLC (EtOAc/hexane (2:98)) t_R= 10.0 min (Hibar Lichrosorb Si 60 (7 μm) column (25 cm × 1 cm)); IR (neat) 3449, 3068, 2957, 1582, 1250, 1186, 1106 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.62 (s, 3 H), 0.81 (d, J = 6.8 Hz, 3 H), 1.40−1.96 (m, 7 H) 7.33−7.40 (m, 6 H), 7.65−7.69 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −5.7 (q), 14.3 (q), 22.3 (t), 32.5 (t), 39.5 (t), 42.2 (d), 127.8 (d, 4 C), 129.3 (d, 2 C), 135.2 (d, 4 C), 135.3 (s, 2 C); MS (rel intensity) m/z 296 (M^+, 1), 281 (20), 214 (8), 197 (100), 158 (50), 137 (70), 120 (20);

HRMS calcd for $C_{19}H_{24}OSi$ 296.1596, found 296.1595. *cis*-**66**: An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.2; HPLC (EtOAc/hexane (2:98)) t_R = 11.3 min (Hibar Lichrosorb Si 60 (7 μm) column (25 cm × 1 cm)); ^{1}H NMR ($CDCl_3$) δ 0.67 (s, 3 H), 0.72 (d, J = 7.2 Hz, 3 H), 1.18−2.29 (m, 7 H) 7.31−7.38 (m, 6 H), 7.56−7.61 (m, 2 H), 7.70−7.79 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.1 (q), 19.4 (q), 21.5 (t), 32.1 (t), 36.3 (t), 45.5 (d), 79.3 (s), 127.8 (d, 4 C), 129.3 (d, 2 C), 135.2 (d, 4 C), 135.5 (s, 2 C); MS m/z (rel intensity) 296 (M^+, 1), 281 (20), 214 (8), 197 (100), 158 (50), 137 (70), 120 (20); HRMS calcd for $C_{19}H_{24}OSi$ 296.1596, found 296.1589.

4-(Diphenylmethylsilyl)-1,8-nonadien-4-ol (63). The solution of **21** (100 mg, 0.34 mmol) and allyl bromide (0.035 mL, 0.4 mmol) was treated with SmI_2 (1 mmol) in THF/HMPA at 32 °C for 2 h gave **63** (96 mg, 84%). An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.25; IR (neat) 3555, 3069, 2935, 1632, 1423, 1250, 1105 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.66 (s, 3 H), 1.26−1.40 (m, 3 H), 1.63−1.72 (m, 2 H), 1.92 (q, J = 6.8 Hz, 2 H), 2.45 (d, J=7.5 Hz, 2 H), 4.86−5.08 (m, 4 H), 5.60−5.79 (m, 2 H), 7.33−7.41 (m, 6 H), 7.70−7.73 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −5.0 (q), 22.8 (t), 34.2 (t), 37.4 (t), 42.0 (t), 69.0 (s), 114.5 (t), 118.8 (t), 127.8 (d, 4 C), 129.3 (d, 2 C), 133.4 (d), 135.2 (s, 2 C), 135.4 (d, 4 C), 138.5 (d); MS m/z (rel intensity) 336 (M^+, 18), 321 (40), 307 (25), 295 (40), 245 (28), 197 (100), 137 (80); HRMS calcd for $C_{22}H_{28}OSi$ 336.1909, found 336.1920.

2-(Diphenylmethyl)-1-phenyl-6-hepten-2-ol (64). The solution of **21** (70 mg, 0.238 mmol) and benzyl bromide (0.035 mL, 0.3 mmol) was treated with SmI_2 (2 mmol) in THF/HMPA at 32 °C for 2 h gave **64** (73 mg, 79%). An oil; TLC (EtOAc/hexane (2:98)) R_f = 0.15; IR (neat) 3536, 3067, 2934, 1633, 1423, 1251, 1107 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.62 (s, 3 H), 1.23 (s, 1 H), 1.29−1.60 (m, 4 H), 1.83−1.93 (q, J = 6.8 Hz, 2 H), 2.92 (d, J = 13.4 Hz, 1 H), 3.12 (d, J=13.4 Hz, 1 H), 4.80−4.89 (m, 2 H), 5.54−5.71 (m, 1 H), 7.06−7.42 (m, 11 H), 7.74−7.79 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −5.2 (q), 23.7 (t), 34.1 (t), 37.6 (t), 42.9 (t), 69.6 (s), 114.4 (t), 126.4 (d), 127.7 (d, 4 C), 128.0 (d, 2 C), 129.2 (d, 2 C), 130.8 (d, 2 C), 135.4 (d, 4 C), 135.5 (d), 136.2 (d, 2 C), 138.3 (d); MS m/z (rel intensity) 386 (M^+, 75), 371 (100), 330 (9), 315 (20), 293 (30), 197 (25), 137 (25).

2-(Diphenylmethylsilyl)-1-[2-(diphenylmethylsilyl)-2-hydroxycyclopentyl]-6-hepten-2-ol (67). The reaction of **21** (200 mg, 0.68 mmol) with SmI_2 (2 mmol) in THF (27 mL) gave **62** (26 mg, 13%), **66** (36 mg, 18%; *cis*/*trans* = 46:54) and **67** (76 mg, 38%; diastereomers **a**/**b**/**c** = 44:44:12). Isomer **a** was isolated by column chromatography on silica gel, and pure isomer **b** was obtained by HPLC. Isomer **a**: An oil; TLC (EtOAc/hexane (10:90)) R_f = 0.27; IR (neat) 3573, 3066, 2938, 1422, 1250, 1106, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.49 (s, 3 H), 0.50 (s, 3 H), 0.91−1.84 (m, 15 H), 2.09−2.17 (m, 2 H), 4.78−4.84 (m, 2 H), 5.50−5.61 (m, 1 H), 7.27−7.39 (m, 12 H), 7.55−7.64 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ −5.4 (q), −5.2 (q), 22.6 (t), 24.0 (t), 32.7 (t), 34.1 (t), 37.6 (t), 38.3 (t), 38.8 (t), 41.7 (d), 70.1 (s), 77.8 (s), 114.4 (t), 127.7 (d, 4 C), 127.8 (d,4 C), 129.2 (d, 2 C), 129.3 (d, 2 C), 133.9 (s), 135.2 (d, 2 C), 135.3 (d, 4 C), 135.4 (d, 2 C), 135.5 (s, 2 C), 135.7 (s), 138.3 (d); FAB-MS m/z (rel intensity) 590 (M^+, 0.2), 571 (0.6), 511 (0.6), 375 (10), 333 (18), 196 (100), 137 (72); HRMS calcd for $C_{38}H_{46}O_2Si_2$ 590.3036, found 590.3036. Isomer **b**: An oil; TLC (EtOAc/hexane (10:90)) R_f = 0.12; IR (neat) 3576, 3066, 2938, 1422, 1249, 1106, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 3 H), 0.57 (s, 3 H), 0.90−1.10 (m, 4 H), 1.41−2.00 (m, 13 H), 4.77−4.83 (m, 2 H), 5.50−5.54 (m, 1 H), 7.26−7.77 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ −5.8 (q), −5.1 (q), 22.4 (t), 23.8 (t), 31.4 (t), 34.2 (t), 37.3 (t), 37.4 (t), 38.6 (t), 42.8 (d), 70.2 (s), 78.4 (s), 114.5 (t), 127.6 (d, 2 C), 127.7 (d, 2 C), 127.8 (d,2 C), 127.9 (d, 2 C), 129.1 (d), 129.2 (d), 129.3 (d), 129.4 (d), 135.1 (d, 2 C), 135.2 (s), 135.3 (d, 4 C), 135.4 (d, 2 C), 135.5 (s, 2 C), 135.7 (s), 138.2 (d); MS m/z (rel intensity) 588 (M^+ − 2, 6), 545 (8), 503 (8), 451 (10), 375 (22), 197 (24), 137 (100); HRMS calcd for $C_{38}H_{44}O_2Si_2$ 588.2880, found 588.2878. Isomer **c** (mixed with isomer **b**): TLC (EtOAc/hexane (10:90)) R_f = 0.12; ^{1}H NMR ($CDCl_3$) δ 0.42 (s), 0.50 (s).

2-[(Tributylstannyl)methyl]cyclopentyl Diphenylmethyl Ether (68). The reaction of **21** (494 mg, 1.68 mmol) and Bu_3SnH (0.68 mL, 2.52 mmol) in deoxygenated benzene according to the general procedure afforded *cis*-**68** (85 mg, 9%), *trans*-**68** (61 mg, 6%), and a *cis*/*trans* (5:1) mixture of **66** (60 mg, 12%) and **62** (225 mg, 45%). *cis*-**68**: A light yellow liquid; IR (neat) 2954, 2922, 1584, 1423, 1248, 1115, 1058, 788, 735, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.65 (s, 3 H), 0.65−1.00 (m, 16 H), 1.15−1.95 (m, 20 H), 4.05 (br q, J = 4.0 Hz, 1 H), 7.25−7.45 (m, 6 H), 7.55−7.65 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −2.3, 9.1, 9.2, 13.7, 21.8, 27.4, 29.3, 31.9, 34.5, 44.0, 78.4, 127.7, 129.5, 134.4, 137.4; MS m/z (rel intensity) 529 ($M^+ - C_4H_9$, 41), 447 (48), 259 (99), 197 (100), 149 (10), 84 (45), 49 (54); HRMS calcd for $C_{27}H_{41}OSiSn$ 529.1949; found 529.1946. *trans*-**68**: A light yellow liquid; IR (neat) 2954, 2922, 1584, 1457, 1423, 1248, 1115, 789, 735, 719, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.67 (s, 3 H), 0.70−1.00 (m, 16 H), 1.15−2.10 (m, 20 H), 3.74 (br q, J = 6.0 Hz, 1 H), 7.25−7.45 (m, 6 H), 7.55−7.65 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −2.2, 9.2, 13.4, 13.7, 21.2, 27.4, 29.2, 32.3, 33.9, 46.4, 83.6, 127.7, 129.6, 134.4, 137.0; MS m/z (rel intensity) 529 ($M^+ - C_4H_9$, 83), 447 (38), 331 (22), 255 (22), 197 (100), 177 (45), 137 (20), 121 (16), 81 (15); HRMS calcd for $C_{27}H_{41}OSiSn$ 529.1949, found 529.1957.

5-Hydroxy-1,5-bis(trimethylsilyl)pentanone (69) and 2,6-Bis(trimethylsilyl)-4,5-dihydro-6*H*-pyran (75). The reaction of 1,5-bis(trimethylsilyl)-1,5-pentanedione **28** (200 mg, 0.81 mmol) with SmI_2 (2 mmol) in THF/HMPA at 18 °C for 12 h gave **69** (20 mg, 10%) and **75** (112 mg, 61%). Compound **69** was unstable and converted to **75** on standing. **69**: An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.1; ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 18 H), 1.65−1.85 (m, 4 H), 2.56 (t, J = 7.0 Hz, 2 H), 3.71 (t, J = 6.6 Hz, 1 H). **75**: An oil; TLC (EtOAc/hexane (5:95)) R_f = 0.25; IR (neat) 2958, 2917, 1619, 1248, 1082, 1038, 1011 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 9 H), 0.03 (s, 9 H), 1.62−1.78 (m, 2 H), 1.91−2.04 (m, 2 H), 3.40 (dd, J = 11.1, 3.2 Hz, 1 H), 4.90−4.94 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ −4.1 (q, 3 C), −2.5 (q, 3 C), 21.3 (t), 23.4 (t), 69.1 (d), 109.2 (d), 162.0 (s); MS m/z (rel intensity) 228 (M^+, 10), 171 (2), 155 (100), 147 (31), 116 (18), 101 (12), 73 (60); HRMS calcd for $C_{11}H_{24}OSi_2$ 228.1366, found 228.1368.

6-Hydroxy-1,6-bis(trimethylsilyl)hexanone (70), 1,6-Bis(trimethylsilyl)-1,6-hexanediol (73), and 1-(Trimethylsilyl)-2-[(trimethylsilyl)carbonyl]cyclopentanol (77). The reaction of 1,6-bis(trimethylsilyl)-1,6-hexanedione **30** (150 mg, 0.77 mmol) with SmI_2 (2 mmol) in THF at 20 °C for 1 h gave **70** (25 mg, 13%), **73** (20 mg, 9%), and **77** (92 mg, 46%). **70**: An oil; TLC (EtOAc/hexane (15:85)) R_f = 0.28; IR (neat) 3400, 2953, 2857, 1640, 1247, 841, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 0.09 (s, 9 H), 1.25−1.57 (m, 7 H), 2.59 (t, J = 6.6 Hz, 2 H), 3.27 (dd, J = 9.1, 4.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −3.9 (q, 3 C), −3.1 (q, 3 C), 21.6 (t), 26.3 (t), 33.1 (t), 48.2 (t), 65.5 (d), 248.6 (s); MS m/z (rel intensity) 242 (M^+ − 18, 6), 169 (58), 147 (30), 129 (20), 111 (2), 85 (1), 73 (100). **73**: Two isomers, solid; mp 69−73 °C; TLC (EtOAc/hexane (15:85)) R_f = 0.1; IR (KBr) 3413, 2912, 1242, 1057, 1011, 916, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 18 H), 1.19−1.50 (m, 10 H), 3.26 (t, J = 6.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −3.9 (q, 12 C), 26.4 (t, 2 C), 26.7 (t, 2 C), 33.3 (t, 2 C), 33.4 (t, 2 C), 65.8 (d, 2 C), 66.0 (d, 2 C); MS m/z (rel intensity) 263 (M^+ + 1, 15), 245 (8), 226 (12), 171 (10), 147 (22), 136 (18), 73 (100); HRMS calcd for $C_{12}H_{29}O_2Si_2$ 261.1706, found 261.1694. **77**: An oil; TLC (EtOAc/hexane (15:85)) R_f = 0.45; IR (neat) 3400, 2957, 2901, 1620, 1249, 840, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.05 (s, 9 H), 0.18 (s, 9 H), 1.51−1.80 (m, 4 H), 1.94−2.05 (m, 2 H), 3.11 (dd, J = 10.6, 8.1 Hz, 1 H), 4.13−4.94 (s, 1 H); ^{13}C NMR (acetone-d_6) δ −3.2 (q, 3 C), −2.9 (q, 3 C), 23.6 (t), 28.6 (t), 38.2 (t), 61.0 (d), 77.7 (s), 257.3 (s); MS m/z (rel intensity) 258 (M^+, 10), 230 (2), 217 (4), 157 (10), 147 (16), 117 (2), 73 (100); HRMS calcd for $C_{12}H_{26}O_2Si_2$ 258.1471, found 258.1487.

7-Hydroxy-1,7-bis(trimethylsilyl)octanone (71) and 1,8-Bis(trimethylsilyl)-1,8-hexanediol (74). The reaction of 1,8-bis(trimethylsilyl)-1,8-hexanedione (**31**) (200 mg, 0.69 mmol) with SmI_2 (2 mmol) in THF for 1 h gave **71** (105 mg, 53%), and **74** (72 mg, 36%). **71**: An oil; TLC (EtOAc/hexane (1:90)) R_f = 0.25; IR (neat) 3438, 2926, 2853, 1633, 1245, 841, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 0.16 (s, 9 H), 1.22−1.50 (m, 11 H), 2.55 (t, J = 7.2 Hz, 2 H), 3.25 (t, J = 6.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −3.9 (q, 3 C), −3.1 (q, 3 C), 22.0 (t), 26.6 (t), 29.3 (t), 29.4 (t), 33.4 (t), 48.4 (t), 65.9 (d), 248.6 (s); MS m/z (rel intensity) 243 (M^+ − 45, 1), 217 (2), 185 (3), 165 (5), 147 (13), 129 (20), 73 (100); HRMS calcd for $C_{14}H_{31}O_2Si_2$ 287.1863, found 287.1864. **74**: Two isomers, solid; mp 79−

84 °C; TLC (EtOAc/hexane (10:90)) $R_f = 0.15$; IR (KBr) 3358, 2923, 2850, 1372, 1244, 1054, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 18 H), 1.21−1.47 (m, 14 H), 3.25 (t, $J = 6.6$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −3.9 (q, 12 C), 26.7 (t, 2 C), 26.8 (t, 2 C), 29.4 (t, 2 C), 29.5 (t, 2 C), 33.5 (t, 2 C), 65.9 (d, 4 C). FAB-MS *m/z* (rel intensity) 291 ($M^+ + 1$, 20), 273 (10), 225 (30), 154 (8), 136 (28), 129 (12), 73 (100); HRMS calcd for $C_{14}H_{32}OSi_2$ 272.1992, found 272.1999.

1,5-Bis(diphenylmethylsilyl)-1,5-pentanediol (72) and 2,6-Bis(diphenylmethylsilyl)-4,5-dihydro-6*H*-pyran (76). The reaction of **29** (230 mg, 0.47 mmol) and Bu_3SnH (0.25 mL, 0.94 mmol) in deoxygenated benzene (10 mL) according to the general procedure gave **76** (116 mg, 52%) and a diastereomeric mixture of **72** (28 mg, 12%). **72**: A white solid; mp 103−106 °C; IR (CH_2Cl_2) 3587, 3067, 2926, 1423, 1363, 1110, 1042, 996, 789 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.57 (s, 6 H,), 1.10−1.70 (m, 8 H), 3.84 (m, 2 H), 7.25−7.40 (m, 12 H), 7.40−7.55 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ −6.8, −6.7, 24.2, 24.4, 32.6, 33.3, 64.2, 64.6, 127.9, 129.5, 129.6, 134.6, 134.9, 135.0. Anal. Calcd for $C_{31}H_{36}O_2Si_2$: C, 74.95; H, 7.30. Found: C, 74.43; H, 7.17. **76**: A light yellow oil; IR (neat) 3064, 3043, 1612, 1424, 1251, 1149, 1112, 1080, 1008, 909, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.56 (s, 3 H), 0.62 (s, 3 H), 1.82−2.20 (m, 4 H), 4.10 (t, $J = 7$ Hz, 1 H), 5.10−5.18 (m, 1 H), 7.20−7.49 (m, 12 H), 7.49−7.70 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ −6.6, −5.0, 21.6, 23.6, 68.9, 114.2, 127.6, 127.7, 129.2, 129.3, 134.9, 135.1, 135.2, 135.5, 158.5; MS *m/z* (rel intensity) 476 (M^+, 5), 333 (16), 319 (6), 279 (100), 255 (10), 197 (74), 137 (6); HRMS calcd for $C_{31}H_{32}OSi_2$ 476.1991, found 476.1960.

3-Hydroxy-3-(trimethylsilyl)cyclohexanone (78). The reaction of 1-(trimethylsilyl)-1,5-hexanedione (**33**) (80 mg, 0.43 mmol) with SmI_2 (0.43 mmol) in THF at 22 °C for 10 min gave **78** (45 mg, 56%). An oil; TLC (EtOAc/hexane (20:80)) $R_f =$ 0.22; IR (neat) 3436, 2948, 1704, 1247, 1111, 940, 839 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04 (s, 9 H), 1.07−2.01 (m, 4 H), 2.21−2.47 (m, 4 H); ^{13}C NMR (acetone-d_6) δ −4.5 (q, 3 C), 22.1 (t), 32.1 (t), 41.8 (t), 49.3 (t), 70.3 (s), 210 (s); MS *m/z* (rel intensity) 186 (M^+, 6), 185 (20), 169 (10), 158 (15), 143 (55), 125 (18), 73 (100); HRMS calcd for $C_9H_{18}O_2Si$ 186.1076, found 186.1073.

6-(Trimethylsilyl)-3,4,5,6-tetrahydropyran-2-one (79). The mixture of 1-(trimethylsilyl)-1,5-pentanedione (**37**) and the dihydropyran derivative **38** (85 mg, 0.49 mmol; **37**/**38** = 5/1) was treated with SmI_2 (0.49 mmol) in THF/MeOH (1 mmol) at 28 °C for 5 min gave **79** (67 mg, 79%). An oil; TLC (EtOAc/hexane (20:80)) $R_f = 0.28$; IR (KBr) 2954, 2856, 1730, 1249, 1179, 1034, 842 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.06 (s, 9 H), 1.60−1.94 (m, 4 H), 2.34−2.61 (m, 2 H), 4.04 (dd, $J = 12.1$, 3.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −4.3 (q, 3 C), 20.3 (t), 23.3 (t), 29.6 (t), 75.3 (d), 173.2 (s); MS *m/z* (rel intensity) 157 ($M^+ - 15$, 48), 143 (18), 129 (17), 116 (100), 101 (65), 75 (70), 73 (52); HRMS calcd for $C_8H_{16}O_2Si$ 172.0920, found 172.0911.

Methyl 6-Hydroxy-6-(trimethylsilyl)hexanoate (80). To a solution of SmI_2/THF/MeOH (0.55 mmol/5.5 mL/1 mmol) was added 1-(trimethylsilyl)-1,6-hexanedione (**47**) (93 mg, 0.5 mmol) in THF (1 mL) in one portion at 30 °C under Ar. The reaction was stirred for 30 min and filtered. The filtrate was concentrated, and the residue was purified by silica gel chromatography with elution of EtOAc/hexane (15:85) to give **80** (63 mg, 62%). An oil; TLC (EtOAc/hexane (15:85)) $R_f = 0.1$; IR (neat) 3442, 2950, 1733, 1431, 1244, 1199, 838 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 1.21−1.67 (m, 6 H), 2.29 (t, $J =$ 7.2 Hz, 2 H), 3.27 (t, $J = 7.0$ Hz, 1 H), 3.62 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ −3.9 (q, 3 C), 24.6 (t), 26.2 (t), 32.9 (t), 33.9 (t), 51.4 (q), 65.6 (d), 174.2 (s); MS *m/z* (rel intensity) 203 ($M^+ - 15$, 21), 172 (11), 171 (82), 143 (18), 129 (13), 89 (15), 73 (100); HRMS calcd for $C_9H_{19}O_3Si$ 203.1104, found 203.1105.

1,12-Bis(trimethylsilyl)-6,7-dihydroxydodecane-1,12-dione (81). To a solution of 1-(trimethylsilyl)-1,6-hexanedione (**47**) (180 mg, 0.96 mmol) and *t*-BuOH (0.19 mL, 2 mmol) in THF (5 mL) was added 0.1 M solution of SmI_2/THF (0.9 mmol/9 mL) at −78 °C under Ar. The resulting solution was warmed to 32 °C and stirred for 2 h. The reaction was quenched by addition of Et_2O (20 mL) and filtered. The filtrate was concentrated, and the residue was purified by silica gel chromatography with elution of EtOAc/hexane (15:85) to give **81** (121 mg, 67%) as a mixture of two diastereomers (3:1). An oil; TLC (EtOAc/hexane (15:85)) $R_f = 0.22$; IR (neat) 3442, 2938, 1632, 1247, 1167, 1082, 839 cm^{-1}; ^1H NMR ($CDCl_3$) (major) δ 0.12 (s, 9 H), 0.16 (s, 9 H), 1.23−1.89 (m, 12 H), 2.61 (t, $J = 7.0$ Hz, 4 H), 3.60−3.75 (m, 2 H); MS *m/z* (rel intensity) 374 (M^+, 8), 284 (4), 259 (4), 217 (4), 187 (24), 171 (100), 73 (90); HRMS calcd for $C_{18}H_{38}O_4Si_2$ 374.2308, found 374.2309.

2-(Dimethylphenylsilyloxy)cyclopentanol (82) and *cis*-1,2-Cyclopentanediol (83). The reaction of **46** (335 mg, 1.43 mmol) and Bu_3SnH (0.58 mL, 2.1 mmol) in deoxygenated benzene (14 mL) according to the general procedure afforded *cis*-**82** (70 mg, 21%), *trans*-**82** (61 mg, 18%), and *cis*-**83** (47 mg, 32%) which was identical to a commercially available authentic sample. *cis*-**82**: IR (neat) 3546, 3047, 2959, 2901, 1423, 1250. 1116, 1050, 994, 890, 829, 786, 740, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.41 (s, 3 H), 0.42 (s, 3 H), 1.30−1.45 (m, 1 H), 1.55−1.85 (m, 6 H), 2.63 (d, $J = 4.2$ Hz, 1 H), 3.88 (quintet, $J = 4.2$ Hz, 1 H), 4.01 (td, $J = 7.0$, 4.2 Hz, 1 H), 7.35−7.45 (m, 3 H), 7.55−7.65 (m, 4 H). ^{13}C NMR ($CDCl_3$) δ −1.4, −1.3, 19.8, 30.7, 31.0, 73.4, 75.4, 127.9, 129.7, 133.3, 137.5. Anal. Calcd for $C_{13}H_{20}O_2Si$: C, 66.05; H, 8.53. Found: C, 65.51; H, 8.64. *trans*-**82**: IR (neat) 3367, 2957, 1423, 1249, 1116, 1043, 990, 876, 828, 784, 740, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.39 (s, 6 H), 1.30−2.05 (m, 7 H), 3.86−4.02 (m, 2 H), 7.30−7.40 (m, 3 H), 7.35−7.65 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ −1.4, −1.1, 19.8, 31.1, 31.9, 79.4, 80.2, 127.9, 129.6, 133.4, 138.3. Anal. Calcd for $C_{13}H_{20}O_2Si$: C, 66.05; H, 8.53. Found: C, 66.04; H, 8.83.

7-Hydroxy-7-(dimethylphenylsilyl)heptanal (84). The reaction of **48** (262 mg, 1.00 mmol) and Bu_3SnH (0.269 mL, 1.00 mmol) in deoxygenated benzene (5 mL) according to the general procedure gave **84** (100mg, 38%) as a light yellow liquid. IR (neat) 3458, 2928, 2854, 1717, 1244, 1110, 814, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.31 (s, 3 H), 0.32, (s, 3 H), 1.05−1.65 (m, 8 H), 2.37 (td, $J = 9.0$, 2.0 Hz, 2 H), 3.47 (t, $J = 7.0$ Hz, 1 H), 7.25−7.45 (m, 3 H), 7.45−7.65 (m, 2 H), 9.71 (t, $J =$ 2.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −5.7, −5.5, 22.0, 26.5, 28.9, 33.1, 43.7, 65.3, 127.9, 129.3, 134,0, 136.6, 202.7; MS *m/z* (rel intensity) 263 ($M^+ - 1$, 1), 249 ($M^+ - CH_3$, 0.5), 247 (5), 185 (10), 165 (5), 135 (100), 129 (8), 91 (8), 81 (8), 75 (24), 55 (11); HRMS calcd for $C_{14}H_{21}O_2Si$ 249.1331, found 249.1321.

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Supporting Information Available: NMR spectra (66 pages) of new compounds. This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; ordering information is given on any current masthead page.

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