The Application of Intramolecular Radical Cyclizations of Acylsilanes in the Regiospecific Formation of Cyclic Silyl Enol Ethers

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Acylsilanes with terminal α-stannyl bromide or xanthate functionalities are prepared. α-Stannyl radicals generated from these acylsilanes undergo intramolecular cyclizations to give cyclic silyl enol ethers regiospecifically. The radical processes involve radical cyclization, Brook rearrangement, and β-fragmentation in sequence. A tributylstannyl group serves as the radical leaving group. The newly formed σ-bond and π-bond are located between the same two carbon atoms. This approach is limited to the formation of five-membered rings. In another route, ω-bromo-α-phenylsulfonylacylsilanes are synthesized. The radical cyclizations of these α-sulfonylacylsilanes also give cyclic silyl enol ethers. The phenylsulfonyl moiety is the radical leaving group in this system. Furthermore, the newly formed σ-bond and π-bond are located at adjacent positions sharing a single carbon atom. The latter approach is effective for both five- and six-membered ring formation.

Introduction

Intramolecular cyclizations of radicals with carbonyl groups are known to be reversible processes.[1] To drive these reactions toward the cyclization side, there are two general strategies. One is to trap the cyclized alkoxy radical intermolecularly using excess tributyltin hydride,[2] silanes,[3] or organophosphorus compounds.[4] The use of large excess of triethylborane also improves the cyclization efficiency.[5] This may be attributed to the trapping of the cyclized alkoxy radical by triethylborane.[5b] The other route relies on the presence of some intramolecular processes such that the cyclized alkoxy radicals are diverted to give other products in an irreversible way. The most notorious application in this direction is the ring expansion of 2-oxocyclopentylmethyl radical and systems alike pioneered by research groups of Beckwith and Dowd.[6,7] Radical cyclizations of acylgermanes give rise to cyclic ketones through β-scission of β-germyl alkoxy radicals.[8] Thio- and selenoesters also undergo similar reactions.[9] The complementary acylsilane cyclizations[10] give cyclic alcohols in the form of silyl ethers through irreversible radical-Brook rearrangements[10−12] of β-silyl alkoxy radical intermediates. In the case of tributyltin hydride mediated pinacol coupling developed by Hays and Fu,[13] the cyclized γ-tributylstannyloxy alkoxy radical was trapped via an intramolecular homolytic substitution at tin. A 1,3-stannyl shift from carbon to oxygen is the driving force for the intramolecular cyclizations of α-stannyl radicals with formyl group.[14]

Among the intramolecular radical cyclization reactions of carbonyl compounds, the acylsilane[15] cyclization system (Scheme 1) is unique, in which a new carbon radical

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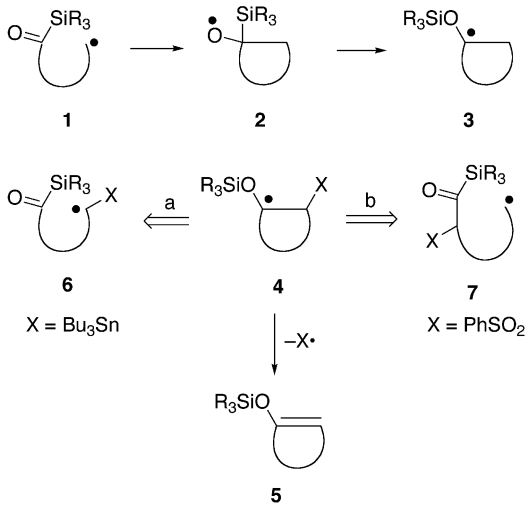
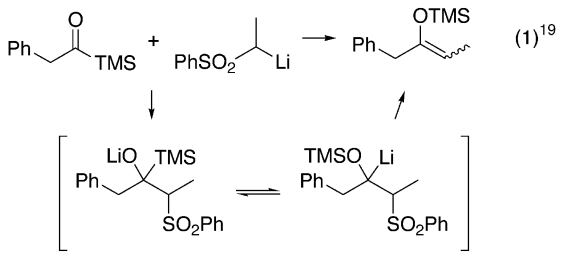
Scheme 1

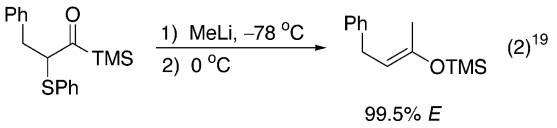


3 is generated after the radical-Brook rearrangement of β-silyl alkoxy radical **2**. By introducing additional structural features, one may utilize the newly generated carbon radical in useful ways. One possibility involves a preexisting radical leaving group X at the β-position of the carbon radical as in radical **4**. A β-scission will occur to generate a silyl enol ether in a regiospecific fashion. In principle, there are two possible approaches to obtain radical **4**. Route a starts from the generation of radical **6** with the radical leaving group attached at the carbon carrying the initial radical. In this direction, we found that the tributylstannyl group served well as the desired radical leaving group.[16] An alternative approach (route b) is to put the radical leaving group at the α-position of the carbonyl group. We found that this route can be realized by the use of phenylsulfonyl group.[17] In this paper, we describe our full investigation of the use of these two approaches in the regiospecific formation of silyl enol ethers.[18,19]

Silyl enol ethers are important synthetic intermediates. There are two widely used methodologies for their synthesis.[18] One is to generate silyl enol ethers from ketones and aldehydes. Another is to prepare them from enones. The latter approach may be the better choice when regiochemically pure silyl enol ethers are required. Both methodologies are performed under basic conditions. Alternatively, silyl enol ethers can be prepared from acylsilanes.[18,19] In this regard, a useful method involves the coupling of an acylsilane with a carbanion bearing α-leaving group (eq 1) was developed by Reich



et al.[19] The initial adduct undergoes a Brook rearrangement, and the resulting silyloxy substituted carbanion fragments to give the silyl enol ether regiospecifically. The leaving group can also be placed at the α-position of the acylsilane as shown in eq 2.[19] Conceptually, the two



routes described in Scheme 1 belong to a neutral radical version of Reich's polar acylsilane chemistry.

Results and Discussion

Intramolecular Cyclizations of α-Stannyl Bromide with Acylsilanes. To explore the route a approach (Scheme 1), we selected a tributylstannyl group as the radical leaving group. There are two reasons for this selection. First, the tributylstannyl group when situated at the β-position of a radical as exemplified in the well-known radical chemistry of allyltributylstannane readily undergoes β-scission.[20] In addition, the tributyltin radical generated through β-scission can be recycled in the radical chain reactions. Second, α-stannyl bromides are a known class of compounds that can be synthesized through established methods.[21]

As shown in Scheme 2, alkylation of 2-silyldithianes **8**[22] with the unprotected 4-chlorobutanol in the presence of excess LDA gave alcohols **9** in excellent yields. Alcohols **9** were oxidized with PCC in dichloromethane to give aldehydes **10** in mild yields. Aldehydes **10** were coupled with tributyltin lithium, and the resulting α-stannyl alcohols were converted to bromides **11** with carbon tetrabromide and triphenylphosphine.[23] As a result of the presence of nucleophilic sulfur atoms in bromides **11**, these compounds are not stable. Therefore, it is better to hydrolyze these bromides immediately with ceric

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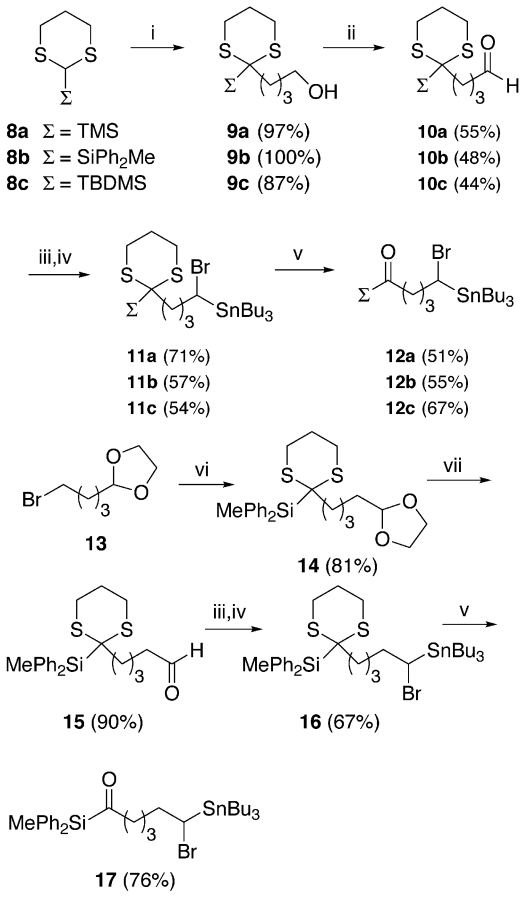
Scheme 2[a]



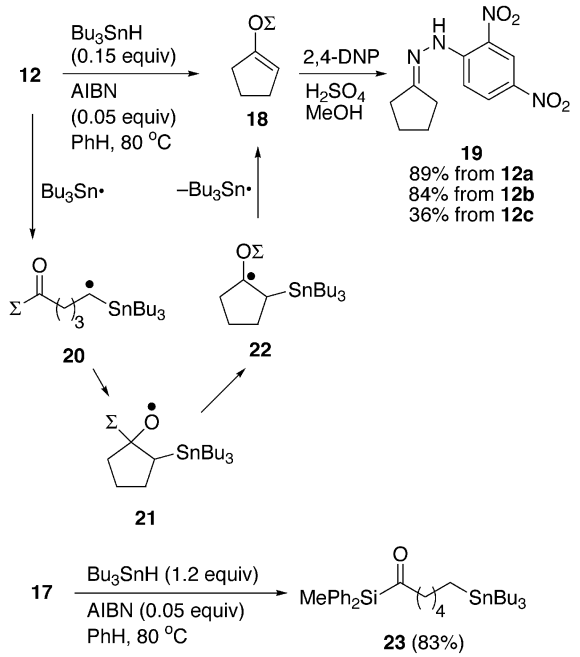
[a] Reagents and conditions: (i) $Cl(CH_2)_4OH$ (2 equiv), LDA (3.6 equiv), THF, −78 °C; (ii) PCC, CH_2Cl_2, 0 °C to room temperature; (iii) Bu_3SnH, LDA, THF, −78 °C; (iv) CBr_4, PPh_3, CH_2Cl_2; (v) CAN, CH_3CN, H_2O; (vi) BuLi, **8b**; (vii) TsOH, THF, H_2O.

ammonium nitrate (CAN) in wet acetonitrile[24] to generate acylsilanes **12**.

For the preparation of the homologous acylsilane **17** (Scheme 2), a slightly different approach was employed. The dithiane **8b**[25] was first alkylated with bromide **13**[26] to obtain acetal **14** (81%). The acetal unit was hydrolyzed in wet THF in the presence of *p*-toluenesulfonic acid to give aldehyde **15** in 90% yield. Acylsilane **17** was then prepared from aldehyde **15** through similar methods as described above.

When acylsilanes **12** were treated with catalytic amount of tributyltin hydride (0.15 equiv) and AIBN (0.05 equiv) in refluxing benzene, we obtained silyl enol ethers **18** (Scheme 3). However, to avoid possible hydrolysis of silyl enol ethers **18** during purification, the products were directly converted to the 2,4-dinitrophenylhydrazone of cyclopentanone (**19**) in 89% and 84% yields for the cyclizations of acylsilanes **12a** and **12b**, respectively. These results indicate that we have obtained silyl enol ethers **18** in good yields. The cyclization reactions occurred through the generation of α-stannyl radicals **20** that cyclized with the acylsilane functionality to give

Scheme 3



β-silyl alkoxy radicals **21**. Radicals **21** were converted to α-silyloxy radicals **22** through a radical-Brook rearrangement. As a result of the presence of a β-stannyl group, radicals **22** underwent a facile β-scission to give silyl enol ethers **18** with concomitant formation of tributyltin radical. Since tributyltin radical was regenerated in the reaction, a catalytic amount of tributyltin hydride (0.15 equiv) was sufficient. The cyclization of acyl-*tert*-butyldimethylsilane **12c** gave low yield (36%) of hydrazone **19** indicating a sluggish cyclization of **12c**. This may be due to the presence of a bulky *tert*-butyldimethylsilyl (TBDMS) group on the carbonyl carbon of the α-stannyl radical **20c**. The steric interaction between the TBDMS and tributylstannyl groups presumably decreased the rate of cyclization significantly. The cyclization of the homologous acylsilane **17** did not occur when a catalytic amount of tributyltin hydride (0.15 equiv) was used. When 1.2 equiv of tributyltin hydride was used, we only isolated 83% of straight reduction product **23** (Scheme 3). Previously, we found that 1,6-radical cyclizations of acylsilanes are sensitive toward steric effect.[10] Presumably, with a bulky α-tributylstannyl radical the cyclization of acylsilane **17** becomes very slow.

To demonstrate the regiospecific nature of this silyl enol ether preparation method, we studied the radical cyclization of acylsilane **29** (Scheme 4). We started from the alkylation of dithiane **8b** with bromide **24**. The resulting acetal **25** (82% yield) was hydrolyzed in aqueous acetic acid to give aldehyde **26** in 74% yield. Originally we tried to prepare bromide **28** according to the methodology described in Scheme 2. However, because of the instability of bromide **28**, we obtained this bromide in very low yield. We then decided to prepare the xanthate **27** because the xanthate moiety may tolerate the presence of the two sulfur atoms in the same molecule.[27] Indeed, when aldehyde **26** was treated with tributyltin lithium followed by trapping the alkoxide intermediate with carbon disulfide and methyl iodide in sequence, we

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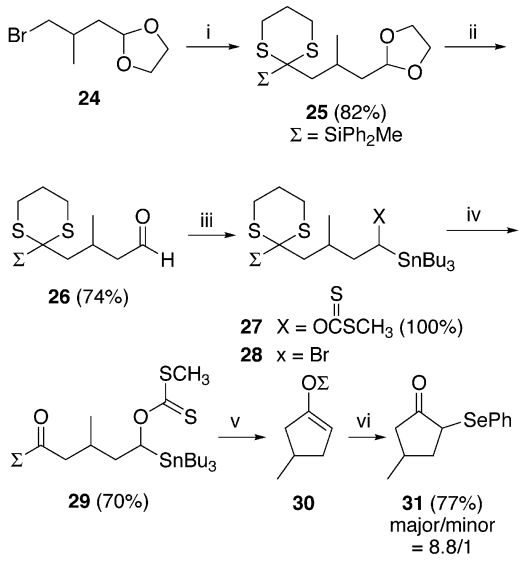
(27) For a recent review about xanthates, see: Zard, S. Z. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 673−685.

Scheme 4[a]

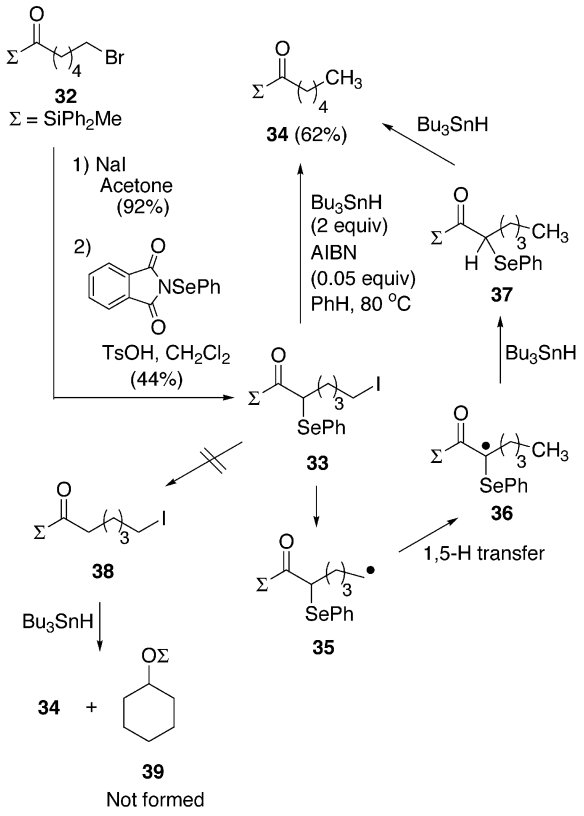


[a] Reagents and conditions: (i) **8b**, BuLi, THF, 0 °C; (ii) AcOH, H_2O; (iii) Bu_3SnH, LDA, THF, −78 °C; CS_2, −78 °C; MeI, −78 °C; (iv) $(CF_3COO)_2IPh$, CH_3CN, H_2O; (v) Bu_3SnH (0.15 equiv), AIBN (0.05 equiv), PhH, 80 °C; (vi) PhSeBr, CH_2Cl_2, −78 °C.

were able to synthesize xanthate **27** in quantitative yield. Hydrolysis of the dithiane moiety in xanthate **27** was carried out with iodobenzenebis(trifluoroacetate)[28] in wet acetonitrile to afford acylsilane **29** (70%). This new route turned out to be a much better way to provide suitable substrates to generate α-stannyl radicals. Treatment of acylsilane **29** with a catalytic amount of tributyltin hydride and AIBN in refluxing benzene led to the formation of silyl enol ether **30**. Simply concentrating the reaction mixture and redesolving the residue in dichloromethane, followed by the addition of phenylselenenyl bromide at −78 °C, gave the selenide **31** in 77% yield as a mixture of *cis*/*trans* isomers.[29] In this way, we demonstrated that silyl enol ether **30** was formed in a regiospecific way. In principle, silyl enol ethers such as **30** can be prepared from 3-substituted cyclopentanones through deprotonation. However, it is difficult to control the regiochemistry of the enolate. Although the use of a bulky base may give the regioisomer such as **30**,[30] the other isomer cannot be eliminated completely. Our method provides a useful approach in addition to other methods.[18,19]

Radical Cyclizations of α-Sulfonylacylsilanes. Although the α-stannyl radical cyclization of acylsilanes is successful for five-membered ring formation, this strategy cannot be applied to six-membered ring formation. The route b approach shown in Scheme 1 may provide an alternative way to accomplish the same goal. In the route b approach, the radical leaving group X is designed at the α-position of the carbonyl. The initial radical **7** does not carry a large substituent at the carbon bearing the radical. Therefore, it will not introduce bad steric interaction between the initial radical and the acylsilane moiety during cyclization as in the case of α-stannyl radical cyclizations.

Scheme 5



The selection of the radical leaving group X is crucial for the success of this strategy. We found that the selenide **33**[31,32] (Scheme 5), prepared from acylsilane **32**, reacted with 2 equiv of tributyltin hydride and gave only straight reduction product **34** in 62% yield. We believe that this result indicates that tributyltin hydride has selectively removed the iodo group to generate the terminal radical **35**. If the phenylselenenyl group were removed first, this would give iodide **38**. We knew that the iodide **38** will further react with tributyltin hydride to give cyclized product **39**.[25] Since we did not observe the formation of silyl ether **39**, it indicates that the iodo group has been removed first. Although the terminal radical **35** was formed, a 1,5-hydrogen atom transfer presumably occurred to give α-carbonyl radical **36**. Acylmethyldiphenylsilane without an α-phenylselenenyl group undergoes 1,6-radical cyclization quite efficiently with little problem associated with the 1,5-hydrogen transfer process.[33] The presence of the phenylselenenyl group probably enhanced the α-radical formation by weakening the α-C−H bond.[34] Hydrogen abstraction of radical **36** from tin hydride gave α-phenylselenenylacylsilane **37** which was further reduced to give acylsilane **34**.

With the above understanding in mind, we picked a phenylsulfonyl group as the radical leaving group. There are several reasons for this choice. First, the phenylsul-

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(29) The isomeric ratio was determined to be 8.8/1 by ^1H NMR integration. However, we did not determine the stereochemistry of the two isomers.
(30) For an example of regioselective deprotonation of 3-substituted cyclopentanone, see: Angle, S. R.; Fevig, J. M.; Knight, S. D.; Marquis, R. W., Jr.; Overman, L. E. *J. Am. Chem. Soc.* **1993**, *115*, 3966−3976.
(31) Cossy, J.; Furet, N. *Tetrahedron Lett.* **1993**, *34*, 7755−7756.
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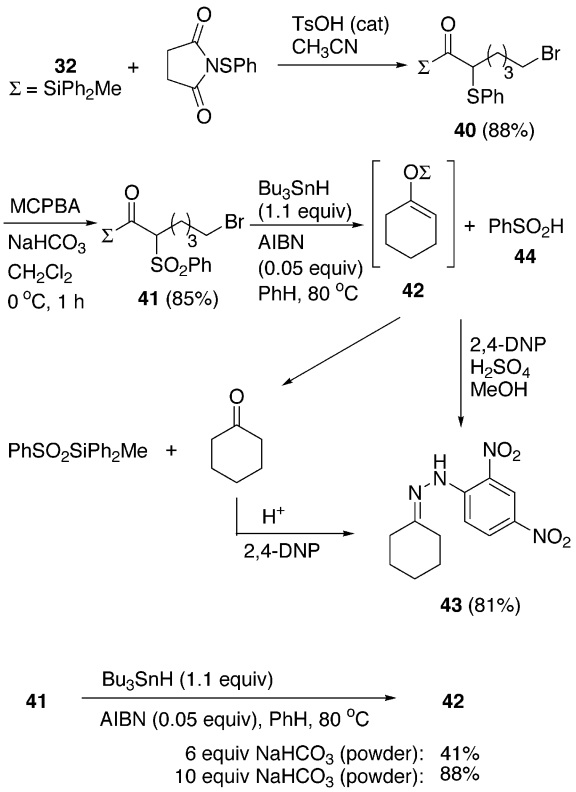
(34) Bordwell, F. G.; Zhang, X.-M.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7623−7629.

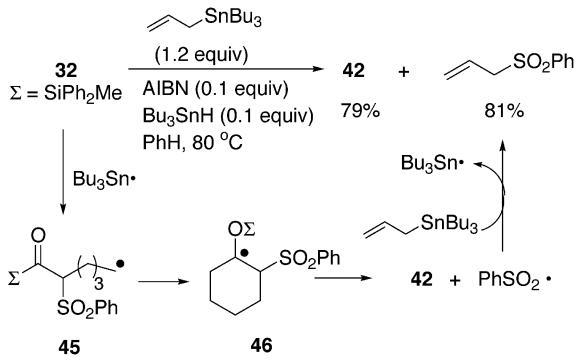
Scheme 6



fonyl group is a well-known radical leaving group exemplified in the radical chemistry of allyl sulfones and vinyl sulfones.[17] Furthermore, radicals adjacent to the strongly electron-withdrawing sulfonyl group will be destabilized.[34,35] We hope that this feature will inhibit the undesired 1,5-hydrogen atom transfer process mentioned above. Moreover, we hope that the presence of an electron-withdrawing group at the α-position will enhance the positive character of the carbonyl carbon. Alkyl-substituted radicals are generally considered as nucleophilic radicals. Therefore, the cyclization rate may be increased. Although there are reports about reductive cleavage of *β*-ketosulfones by tributyltin hydride,[36] the reactions appear to have a short radical chain length,[36a] an indication of a slow process. Therefore, it is possible to find proper substrates to selectively generate the desired radicals without the interference of the *β*-ketosulfone functionality.

We found that the α-phenylthioacylsilane **40** (Scheme 6) could be prepared in 88% yield from the reaction of bromoacylsilane **32** with *N*-phenylthiosuccinimide in acetonitrile catalyzed by *p*-toluenesulfonic acid (0.05 equiv).[37] Oxidation of sulfide **40** was performed using *m*-chloroperbenzoic acid (MCPBA) to afford sulfone **41** in 85% yield. Radical cyclization of sulfone **41** employing tributyltin hydride was expected to give silyl enol ether **42**. However, by examining the crude cyclization mixture with ^{1}H NMR, we were not able to observe the presence of **42**. Gas chromatographic analysis of the crude cyclization mixture showed the presence of cyclohexanone. Addition of a methanol solution of 2,4-dinitrophenylhydrazine (2,4-DNP) and sulfuric acid to the reaction mixture resulted in the isolation of the 2,4-dinitrophenylhydrazone **43** in 81% yield. These results indicate that silyl enol ether **42** was initially formed. However, as a result of the presence of phenylsulfinic acid (**44**) as the byproduct, silyl enol ether **42** likely reacted further with sulfinic acid **44** to produce cyclohexanone as the final product.

Scheme 7



To stop the cyclization reaction at the silyl enol ether stage, one needs to remove the nuisance acid **44** in situ. When we used 6 equiv of freshly ground sodium bicarbonate powder in the cyclization condition, silyl enol ether **42** was isolated in 41% yield through silica gel column chromatography. Further increment of sodium bicarbonate powder to 10 equiv resulted in 88% isolation yield of silyl enol ether **42**. Because we did not isolate any reduction product or cyclization product such as **39** (Scheme 5), we believe that the bromide in sulfone **41** was removed selectively by tributyltin radical in the presence of the *β*-ketosulfonyl group.

There is another way that one can eliminate the formation of sulfinic acid **44**. As shown in Scheme 7, acylsilane **32** was treated with allyltributyltin (1.2 equiv) in the presence of catalytic amount of tributyltin hydride (0.1 equiv) and AIBN (0.1 equiv) to yield silyl enol ether **42** (79%) and allyl phenyl sulfone[38] (81%). This process involves the formation of radical **45** first. Cyclization of **45** followed by radical-Brook rearrangement of the resulting alkoxy radical gave α-silyloxy radical **46**. *β*-Elimination of phenylsulfinyl radical produced silyl enol ether **42**. The phenylsulfinyl radical was trapped by allyltributyltin and converted to allyl phenyl sulfone. Tributyltin radical was formed at the same time and reacted further with acylsilane **32** to continue a new cycle. Without the formation of phenylsulfinic acid (**44**), silyl enol ether **42** was obtained successfully.

This methodology can be employed in five-membered ring formation. As shown in Scheme 8, α-sulfonylacylsilanes **49** and **53** were prepared in high yields from acylsilanes **47**[25] and **51**,[25] respectively, according to the methods described above. Radical cyclization of acylsilane **49** with tributyltin hydride (1.2 equiv) in the presence of large excess of sodium bicarbonate powder (15 equiv) resulted in the formation of silyl enol ether **50**. This silyl enol ether appeared to be quite sensitive toward silica

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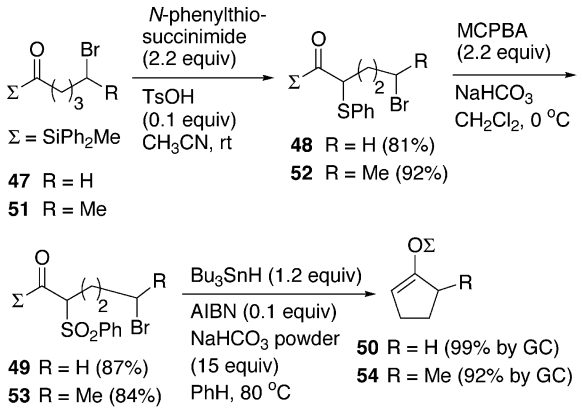
(36) (a) Smith, A. B., III; Hale, K. J.; McCauley, J. P., Jr. *Tetrahedron Lett.* **1989**, *30*, 5579−5582. (b) Giovannini, R.; Petrini, M. *Synlett* **1995**, 973−974. (c) Parsons, A. F.; Pettifer, R. M. *Tetrahedron Lett.* **1996**, *37*, 1667−1670. (d) Wnuk, S. F.; Rios, J. M.; Khan, J.; Hsu, Y.-L. *J. Org. Chem.* **2000**, *65*, 4169−4174.

(37) Huang, C.-H.; Liao, K.-S.; De, S. K.; Tsai, Y.-M. *Tetrahedron Lett.* **2000**, *41*, 3911−3914.

(38) Russell, G. A.; Herold, L. L. *J. Org. Chem.* **1985**, *50*, 1037−1040.

Scheme 8



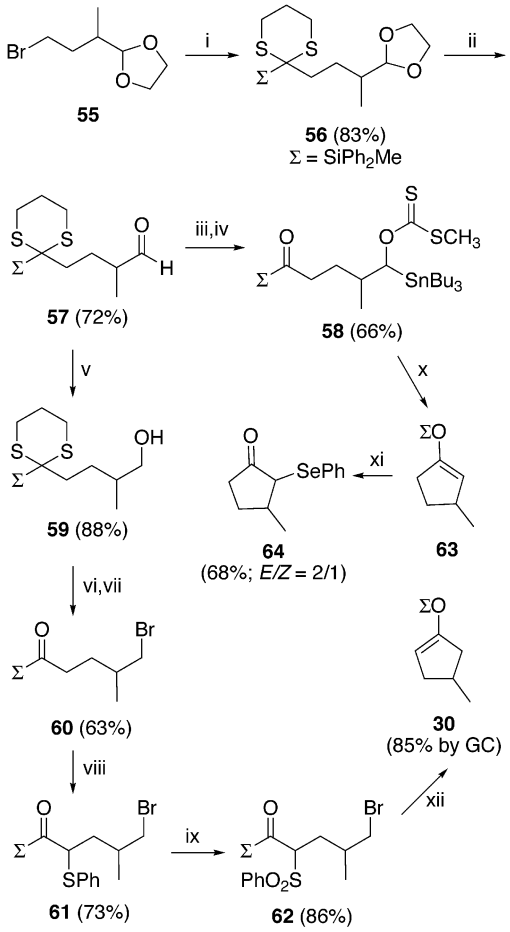
gel column chromatography. We were able to isolate **50** in 52% yield. Gas chromatographic analysis using decane as internal standard showed that silyl enol ether **50** was actually formed in 99% yield.

Radical cyclization of acylsilane **53** under similar condition produced silyl enol ether **54**. Gas chromatographic analysis using tetradecane as internal standard indicated that **54** was formed in 92% yield. For the purpose of analysis, an authentic sample of silyl enol ether **54** was prepared by sequential reactions of 2-methylcyclopentanone with LDA and methyldiphenylsilyl chloride.[39] A mixture of **54** and its regioisomer (GC ratio of 9/1 in favor of **54**) was obtained and separable by gas chromatography (10% SE-30 on Chromosorb W). Gas chromatographic analysis also showed that the silyl enol ether synthesized from radical cyclization is a single isomer corresponding to the kinetic isomer **54** obtained from 2-methylcyclopentanone.

Demonstration of Regiospecific Synthesis of Isomeric Silyl Enol Ethers through a Common Starting Material. With the development of two methods of silyl enol ether synthesis from radical cyclizations of acylsilanes, one can begin with a single starting material and control the regiochemistry of silyl enol ether formation by proper choice of the method. As shown in Scheme 9, alkylations of dithiane **8b** with bromide **55**[40] gave acetal **56** in 83% yield. Hydrolysis of the acetal afforded aldehyde **57** (72%). Conversion of aldehyde **57** to xanthate **58** (66%) was performed using methods described above. On the other hand, reduction of aldehyde **57** with sodium borohydride in ethanol gave alcohol **59** (88%). This alcohol was converted to bromoacylsilane **60** using carbon tetrabromide and triphenylphosphine[41] followed by hydrolysis of the dithiane moiety with CAN in wet acetonitrile.[24] α-Sulfonylacylsilane **62** was prepared from acylsilane **60** through α-sulfenylation[37] and oxidation processes.

Xanthate **58** reacted with catalytic amount of tributyltin hydride (0.15 equiv) in refluxing benzene and yielded silyl enol ether **63**. Without purification of **63**, the crude concentrate of the cyclization reaction mixture was redesolved in dichloromethane and treated with phenylselenenyl bromide at −78 °C to afford selenide **64** (68%) as a mixture of *E*- and *Z*-isomers (*E*/*Z* = 2/1).[42]

Scheme 9[a]



[a] Reagents and conditions: (i) **8b**, BuLi, THF, 0 °C; (ii) AcOH, H_2O; (iii) Bu_3SnH, LDA, THF, −78 °C; CS_2, −78 °C; MeI, −78 °C; (iv) $(CF_3COO)_2IPh$, CH_3CN, H_2O; (v) $NaBH_4$, EtOH/CH_2Cl_2, 0 °C; (vi) CBr_4, PPh_3, CH_2Cl_2, 0 °C; (vii) red HgO, BF_3·OEt_2, H_2O, THF, rt; (viii) *N*-phenylthiosuccinimide, TsOH, CH_3CN, rt; (ix) MCPBA (2.2 equiv), $NaHCO_3$, CH_2Cl_2, 0 °C; (x) Bu_3SnH (0.15 equiv), AIBN (0.05 equiv), PhH, 80 °C; (xi) PhSeBr, CH_2Cl_2, −78 °C; (xii) Bu_3SnH (1.2 equiv), AIBN (0.1 equiv), $NaHCO_3$ powder (15 equiv), PhH, 80 °C.

In comparison, α-sulfonylacylsilane **62** was treated with 1.2 equiv of tributyltin hydride along with catalytic amount of AIBN (0.1 equiv) and excess sodium bicarbonate fine powder (15 equiv) in refluxing benzene. The crude reaction mixture was analyzed by gas chromatography using tetradecane as internal standard, and the yield of silyl enol ether **30** was determined as 85%. ^{1}H NMR analysis showed that a single isomer was formed. An authentic sample of a mixture of silyl enol ethers **30** and **63** (**30**/**63** = 3/2) was prepared from 3-methylcyclopentanone through deprotonation and silylation. The two isomers can be differentiated by their ^{1}H NMR signals (in $CDCl_3$) of the vinyl hydrogens. The characteristic signal of **30** appears at δ 4.50 (br s), and that of **63** appears at δ 4.54 (br s). It should be noted that when we used 10 equiv of sodium bicarbonate in the cyclization of acylsilane **62**, a 9/1 mixture of silyl enol ethers **30** and **63** in favor of **30** was obtained. We assumed that this is due to slow scavenge of phenylsulfinic acid (**44**) by sodium bicarbonate. The small amount of acid reacted with the silyl enol ether and yielded 3-methylcyclopentanone. Silyl enol ether **30** may exchange the silyl group with 3-methylcyclopentanone or its enol form (Scheme 10) to produce the isomeric silyl enol ether **63**. When 15 equiv

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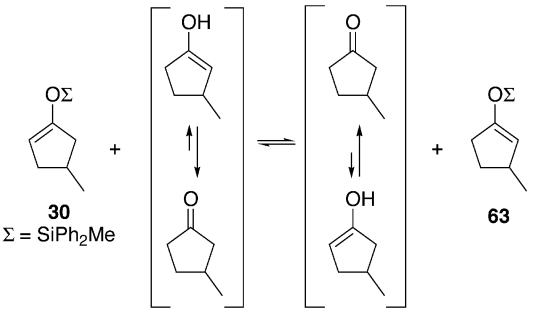
(41) Castro, B. R. *Org. React.* **1983**, *29*, 1−162.
(42) Toru, T.; Okumura, T.; Ueno, Y. *J. Org. Chem.* **1990**, *55*, 1277−1280.

Scheme 10



of sodium bicarbonate was used, phenylsulfinic acid (**44**) can be removed more efficiently. Therefore, isomerization of silyl enol ether **30** was not observed.

Conclusions

In this study, we have successfully developed two routes in the synthesis of regiospecific cyclic silyl enol ethers employing intramolecular radical cyclizations of acylsilanes. Both approaches involve β-fragmentation of the cyclized α-silyloxy radical intermediates. The cyclizations of acylsilanes carrying terminal α-tributylstannyl bromide or xanthate functionalities adopt the tributylstannyl group as the radical leaving group for the β-fragmentation. This approach works only for five-membered ring formation. The other approach uses α-phenylsulfonylacylsilanes as the substrates. The α-phenylsulfonyl group serves as the radical leaving group. Although the latter approach works well for both five- and six-membered ring formations, the concomitant formation of phenylsulfinic acid causes some trouble. This side product can be removed by the use of excess (15 equiv) sodium bicarbonate powder. Because of the difference in the direction of bond formation, the two radical approaches are complementary regarding the regiochemistry of cyclic silyl enol ether formation. Within the same route, tuning the position of the substituents on the acylsilane backbone will also lead to the formation of the desired regioisomer.

This study extended the synthetic utility of acylsilanes.[15] Although there are many methods for the preparation of silyl enol ethers, most of them employ strongly basic conditions.[18] Our radical approach works under neutral conditions and may offer some advantages when base-sensitive functionalities are present. However, the efficiency of our method depends on how easily the acylsilanes can be synthesized, and it is successful only for five- and six-membered cyclic silyl enol ethers.

Experimental Section

Melting points are uncorrected. ^{1}H NMR spectra were recorded at 200 or 300 MHz; ^{13}C NMR spectra were recorded at 50 or 75 MHz. Tetramethysilane (δ = 0 ppm) or $CHCl_3$ (δ = 7.24 ppm) were used as internal standards, and $CDCl_3$ was used as the solvent. Benzene and THF were distilled from sodium/benzophenone ketyl under N_2. Diisopropylamine and acetonitrile were dried with CaH_2 and distilled. The benzene used for cyclization reactions was deoxygenated by passing a gentle stream of argon through it for 0.5 h before use. All reactions were performed under a blanket of N_2 or Ar. Lobar LiChroprep Si 60 (40−63 μm) prepacked columns purchased from Merck were used for medium-pressure liquid chromatography (MPLC). Gas chromatography was performed on a Shimadzu GC-8A apparatus with TCD using a 3.3 mm × 2 m column of 10% SE-30 on Chromosorb W (AW-DMCS), 80−100 mesh, and hydrogen as carrier gas. Aldehydes **10** were prepared from the corresponding 2-silyl-1,3-dithianes **8** according to the general procedure described before.[43]

General Procedure for the Preparation of Acylsilanes 12. 5-Bromo-5-tributylstannyl-1-(methyldiphenylsilyl)-1-pentanone (12b). To a solution of 0.34 mL (2.4 mmol) of diisopropylamine in 2 mL of dry THF cooled at 0 °C under argon was added over 10 min a solution of 1.5 N butyllithium in hexane (1.6 mL, 2.4 mmol). The resulting solution was stirred at the same temperature for 30 min followed by the addition of 0.64 mL (2.4 mmol) of tributyltin hydride over 10 min. The reaction mixture was stirred for another 30 min at 0 °C and then cooled in a dry ice/acetone bath. To this cold solution was added dropwise over 1 h a solution of 773 mg (2.0 mmol) of aldehyde **10b** in 2 mL of dry THF. The reaction mixture was stirred at the same temperature for 1 h and then poured into a mixture of ether and a 0.05 N ammonium chloride solution. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The resulting residue and 1.06 g (3.2 mmol) of carbon tetrabromide were dissolved in 5 mL of dichloromethane and then cooled in an ice/water bath. To this solution was added dropwise over 20 min a solution of 839 mg (3.2 mmol) of triphenylphosphine in 2.5 mL of dichloromethane. The resulting mixture was stirred at room temperature for 1 h and filtered over a short pad of silica gel column (washed with hexane/ethyl acetate, 9/1). The filtrate was concentrated, and the residual oil was chromatographed with MPLC over a Lobar size B column (eluted with hexane/ethyl acetate, 98/2) to give 771 mg (57%) of **11b** as a pale yellow liquid: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.78 (s, 3 H), 0.83−0.95 (two overlapped t, J = 7 Hz, at 0.89 and 0.93, 15 H), 1.29 (sextet, J = 7 Hz, 6 H), 1.41−2.28 (m, 14 H), 2.42 (dt, J = 13.5, 4 Hz, 2 H), 2.98 (ddd, J = 13.5, 11, 4 Hz, 2 H), 3.48 (dd, J = 9.5, 5 Hz, 1 H), 7.28−7.42 (m, 6 H), 7.78−7.84 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −3.9, 9.9 (J_{C-Sn} = 315 Hz), 13.6, 24.0, 24.6, 27.3 (J_{C-Sn} = 60 Hz), 27.6, 28.9 (J_{C-Sn} = 20 Hz), 37.2, 38.0, 39.0, 127.5, 129.6, 134.2, 135.9. Bromide **11b** was not stable at room temperature and should be hydrolyzed as soon as possible. To a mixture of 771 mg (1.04 mmol) of **11b**, 71 mg (0.85 mmol) of sodium bicarbonate, and 48 mg of Celite in dichloromethane/acetonitrile (3 mL/2 mL) cooled at −15 °C (dry ice/carbon tetrachloride bath) was added dropwise over 10 min a solution of 1.72 g (3.1 mmol) CAN in aqueous acetonitrile (acetonitrile/water = 15 mL/1 mL). The resulting mixture was stirred at the same temperature for another 10 min, diluted with ether, and filtered. The filtrate was partitioned between ether and water. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed over silica gel (eluted with hexane/ethyl acetate, 98/2) to give 377 mg (55%) of **12b** as a pale yellow oil: IR (neat) 1634 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.74 (s, 3 H), 0.78−1.10 (m, 15 H), 1.28 (sextet, J = 7 Hz, 6 H), 1.37−1.67 (m, 6 H), 1.67−1.95 (m, 4 H), 2.65 (br t, J = 7 Hz, 2 H), 3.49 (dd, J = 8.5, 6 Hz, 1 H), 7.27−7.48 (m, 6 H), 7.50−7.62 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ −5.3, 9.9 (J_{C-Sn} = 315 Hz), 13.6, 22.6, 27.3 (J_{C-Sn} = 60 Hz), 28.9 (J_{C-Sn} = 20 Hz), 37.0, 39.1, 48.5, 128.1, 130.1, 132.7, 135.0, 243.8. Anal. Calcd for $C_{30}H_{47}BrOSiSn$: C, 55.40; H, 7.28. Found: C, 55.65; H, 6.87.

General Procedure for Intramolecular Radical Cyclizations of α-Stannyl Bromides. Cyclization of 12b. To a refluxing solution of 325 mg (0.50 mmol) of **12b** in 2.5 mL of benzene was added via syringe pump over 1 h a solution of 19 μL (0.060 mmol) of tributyltin hydride and 4.0 mg (0.024 mmol) of AIBN in 2.5 mL of benzene. The resulting solution was heated for 1 h and then cooled to room temperature. To the resulting reaction mixture was added a solution of 197 mg (1.0 mmol) 2,4-dinitrophenylhydrazine in 5 mL of methanol, and 0.25 mL of 98% sulfuric acid. The resulting mixture was stirred overnight, poured into a saturated sodium bicarbonate solution, and then extracted with ether. The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed over silica

(43) Chuang, T.-H.; Fang, J.-M.; Jiaang, W.-T.; Tsai, Y.-M. *J. Org. Chem.* **1996**, *61*, 1794−1805.

gel (eluted with hexane/ethyl acetate, 9/1) to give 110 mg (84%) of cyclopentanone 2,4-dinitrophenylhydrazone (**19**) as an orange solid: mp 148−150 °C (lit.[44] 146−148 °C).

2-(4-Bromo-3-methylpropyl)-1,3-dioxolane (24). Ozone gas was bubbled into a solution of 3.87 g (23.7 mmol) of 5-bromo-4-methyl-1-pentene[45] in 20 mL of methanol cooled at −78 °C until the solution turned into pale blue. To the reaction mixture was added 20 mL of dimethyl sulfide, and the resulting solution was stirred at room temperature for 3 days. The resulting reaction mixture was partitioned between ether and water. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. To the resulting residue was added 1.44 mL of ethylene glycol, 380 mg (2.0 mmol) of *p*-toluenesulfonic acid, and 30 mL of benzene. The resulting mixture was heated under reflux for 24 h, and water was removed via a Dean−Stark apparatus. The reaction mixture was partitioned between ether and water. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was distilled to give 3.87 g (78%) of **24** as a colorless liquid: bp 72−73 °C/1.5 mmHg; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.08 (d, J = 6.6 Hz, 3 H), 1.52−1.70 (m, 1 H), 1.71−1.80 (m, 1 H), 1.95−2.16 (m, 1 H), 3.32−3.58 (m, 2 H), 3.72−4.01 (m, 4 H), 4.89 (t, J = 5 Hz, 1 H). Anal. Calcd for $C_7H_{13}BrO_2$: C, 40.21; H, 6.27. Found: C, 39.89; H, 6.10.

2-(2-Methyl-3-(2,5-dioxacyclopentyl)propyl)-2-(methyldiphenylsilyl)-1,3-dithiane (25). To a solution of 2.53 g (8.0 mmol) of **8b** in 8 mL of dry THF under argon cooled at 0 °C was added dropwise over 10 min a solution of 1.53 N butyllithium in hexane (5.5 mL, 8.4 mmol). The resulting solution was stirred at 0 °C for 20 min followed by the addition of 1.3 mL (8.0 mmol) of **24** over a period of 20 min. The resulting mixture was stirred at room temperature for 2 h and then partitioned between ether and water. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residual oil was chromatographed with MPLC over a Lobar size B column (eluted with hexane/ethyl acetate, 9/1) to give 2.90 g (82%) of **25** as a white solid: mp 87.5−88.0 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.85 (s, 3 H), 0.95 (d, J = 6.5 Hz, 3 H), 1.38 (ddd, J = 13.5, 8.5, 4.5 Hz, 1 H), 1.77 (dt, J = 13.5, 4.5 Hz, 1 H), 1.82−2.15 (m, 4 H), 2.25 (dd, J = 14.5, 4.5 Hz, 1 H), 2.44 (dt, J = 13.5, 4.5 Hz, 2 H), 2.91 (br t, J = 13.5 Hz, 2 H), 3.69−3.90 (m, 4 H), 4.63 (t, J = 5.5 Hz, 1 H), 7.30−7.43 (m, 6 H), 7.83 (d, J = 7 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.0, 21.7, 24.3, 24.4, 28.2, 39.0, 41.8, 44.9, 64.2, 64.4, 103.4, 127.4, 129.3, 134.6, 135.8. Anal. Calcd for $C_{24}H_{32}O_2S_2Si$: C, 64.82; H, 7.25. Found: C, 64.49; H, 7.17.

3-Methyl-4-(1-methyldiphenylsilyl-2,6-dithiacyclohexyl)-butanal (26). A solution of 2.90 g (6.53 mmol) of **25** in 7 mL of acetic acid and 1 mL of water was heated at 60 °C overnight. The resulting mixture was carefully added to a saturated sodium bicarbonate solution followed by extraction with ether. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed over silica gel (eluted with hexane/ethyl acetate, 9/1) to give 1.933 mg (74%) of **26** as a white solid: mp 85−87 °C; IR (CH_2Cl_2) 1712 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.83 (d, J = 6 Hz, 3 H), 0.84 (s, 3 H), 1.80−2.35 (m, 6 H), 2.35−2.63 (m, 3 H), 2.98−3.01 (m, 2 H), 7.28−7.46 (m, 6 H), 7.71−7.87 (m, 4 H), 9.35 (t, J = 1.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −3.9, 22.1, 24.3, 24.4, 24.5, 27.7, 39.0, 43.9, 51.6, 127.6, 129.7, 134.3, 135.8, 202.4; HRMS calcd for $C_{22}H_{28}OS_2Si$ m/z 400.1351, found 400.1351.

General Procedure for the Preparation of Dithiane Xanthates. *O*-[1-Tributylstannyl-3-methyl-4-(1-methyldiphenylsilyl-2,6-dithiacyclohexyl)]butyl *S*-Methyl Dithiocarbonate (27). To a solution of 0.16 mL (1.1 mmol) diisopropylamine in 1 mL of dry THF cooled at 0 °C under argon was added over 10 min a solution of 1.5 N butyllithium in hexane (0.73 mL, 1.1 mmol). The resulting solution was stirred at the same temperature for 10 min, followed by the addition of 0.30 mL (1.1 mmol) of tributyltin hydride over 10 min. The reaction mixture was stirred at the same temperature for another 30 min and then cooled in an dry ice/acetone bath. To the cold solution was added dropwise over 30 min a solution of 403 mg (1.0 mmol) of **26** in 1 mL of THF. The resulting mixture was stirred at the same temperature for 1 h, followed by the addition of 68 μL (1.1 mmol) of carbon disulfide, and then warmed to room temperature. The reaction mixture was stirred at room temperature for 30 min and then cooled in a dry ice/acetone bath. To the cold mixture was added 94 μL (1.5 mmol) of methyl iodide, and the reaction mixture was warmed to room temperature. The resulting mixture was stirred at room temperature for 1 h and partitioned between ether and water. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed over silica gel (eluted with hexane/ethyl acetate, 98/2) to give 716 mg (100%) of **27** as a yellow oil. This material is a 1:1 mixture of two diastereomers: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.65−1.00 (m, 21 H), 1.10−2.50 (m, 21 H), 2.49 (s, 1.5 H, S-Me of one isomer), 2.54 (s, 1.5 H, S-Me of another isomer), 2.75−3.04 (m, 2 H), 5.69−5.89 (m, 1 H), 7.26−7.44 (m, 6 H), 7.73−7.90 (m, 4 H). Anal. Calcd for $C_{36}H_{58}OS_4SiSn$: C, 55.30; H, 7.48. Found: C, 54.89; H, 7.49.

General Procedure for the Hydrolysis of Dithiane Xanthates. *O*-(1-Tributylstannyl-3-methyl-5-methyldiphenylsilyl-5-oxopentyl) *S*-Methyl Dithiocarbonate (29). To a mixture of 781 mg (1.0 mmol) of **27** and 126 mg (1.5 mmol) of sodium bicarbonate in 4.5 mL of THF, 4.5 mL of acetonitrile, and 1 mL of water was added over 5 min a solution of 602 mg (1.4 mmol) of iodobenzenebis(trifluroacetate) in 2 mL of acetonitrile. The resulting mixture was stirred at room temperature for 15 min and then partitioned between ether and water. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed over silica gel (eluted with hexane/ethyl acetate, 98/2) to give 483 mg (70%) of **29** as a yellow oil. This material is a 1:1 mixture of two isomers: IR (CH_2Cl_2) 1633 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.70−1.10 (m, 21 H), 1.23−1.70 (m, 13 H), 2.02−2.28 (m, 2 H), 2.34−2.83 (m overlapped with two s at 2.53 and 2.55, 5 H), 5.82−5.89 (m, 0.5 H, OCH of one isomer), 5.89−5.95 (m, 0.5 H, OCH of another isomer), 7.27−7.48 (m, 6 H), 7.50−7.68 (m, 4 H). Anal. Calcd for $C_{33}H_{52}O_2S_2SiSn$: C, 57.31; H, 7.58. Found: C, 57.39; H, 7.58.

Radical Cyclization of 29 and Direct Conversion to Selenide. 4-Methyl-2-(phenylselenenyl)cyclopentanone (31). According to the general cyclization procedure of α-stannyl bromides, 483 mg (0.70 mmol) of **29** was cyclized with tributyltin hydride (29 μL, 0.11 mmol) and AIBN (6 mg, 0.037 mmol) in benzene. At the end of the cyclization, the solvent was removed in vacuo, and the residue was taken up into 2 mL of dichloromethane. The solution was cooled in a dry ice/acetone bath followed by the addition of a solution of 164 mg (0.70 mmol) of phenylselenenyl bromide in 2 mL of dichloromethane over a period of 10 min. The resulting solution was stirred at the same temperature for 1 h and then partitioned between ether and water. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. To the residue was added a few drops of wet triethylamine,[46] and the resulting mixture was chromatographed over silica gel (eluted with hexane/ethyl acetate, 8.8/1) to give 136 mg (77%) of **31** as a pale yellow oil. This material is a 9:1 mixture of two isomers: IR (neat) 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.08 (d, J = 6.5 Hz, 3 H), 1.48−2.02 (m, 2 H), 2.02−2.25 (m, 1 H), 2.35−2.68 (m, 2 H), 3.72 (dd, J = 11, 8.5 Hz, 0.12 H, SeCH of the minor isomer), 3.82 (br d, J = 6.5 Hz, 0.88 H, SeCH of the major isomer), 7.18−7.46 (m, 3 H), 7.48−7.70 (m, 2 H); HRMS calcd for $C_{12}H_{14}OSe$ m/z 254.0210, found 254.0215.

General Procedure for α-Sulfenylation of Acylsilanes. 6-Bromo-1-(methyldiphenylsilyl)-2-phenylsulfenyl-1-hexanone (40). A mixture of 2.10 g (5.60 mmol) of **32**, 2.55 g (12.3 mmol) of *N*-phenylthiosuccinimide, and 106 mg (0.559 mmol) of *p*-toluenesulfonic acid in 28 mL of dry acetonitrile was stirred under argon at room temperature for 5.5 h. The

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resulting mixture was partitioned between ether and water. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residual oil was chromatographed with MPLC over a Lobar size B column (eluted with hexane/ethyl acetate, 95/5) to give 2.39 g (88%) of **40** as a greenish yellow oil: IR (neat) 1623 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.89 (s, 3 H), 1.38−1.45 (m, 1 H), 1.45−1.60 (m, 2 H), 1.66−1.84 (m, 3 H), 3.27 (t, J = 6.7 Hz, 2 H), 3.86 (t, J = 7.0 Hz, 1 H), 7.03 (br d, J = 7.0 Hz, 2 H), 7.10−7.23 (m, 3 H), 7.34−7.48 (m, 6 H), 7.62−7.70 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −3.9 (q), 25.7 (t), 27.2 (t), 32.4 (t), 33.2 (t), 60.5 (d), 127.9 (d), 128.0 (d), 128.1 (d), 128.8 (d), 130.0 (d), 131.5 (s), 132.8 (s), 133.0 (d), 135.2 (d), 231.9 (s). Anal. Calcd for $C_{25}H_{27}BrOSSi$: C, 62.10; H, 5.63. Found: C, 61.16; H, 5.61.

General Procedure for the Oxidation of α-Phenylsufenylacylsilanes. 6-Bromo-1-(methyldiphenylsilyl)-2-phenylsulfonyl-1-hexanone (41). To a mixture of 2.39 g (4.94 mmol) of **40** and 4.15 g (49.4 mmol) of sodium bicarbonate in 33 mL of dichloromethane cooled in an ice/water bath was added 2.68 g (10.9 mmol) of MCPBA (70%). The resulting mixture was stirred at 0 °C for 30 min, quenched by stirring with 146 mg (0.987 mmol) of sodium thiosulfate for 5 min, and then partitioned between dichloromethane and water. The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residual oil was chromatographed with MPLC over a Lobar size B column (eluted with hexane/ethyl acetate, 9/1 and then 8/2) to give 2.16 g (85%) of **41** as a greenish yellow oil: IR (neat) 1640 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.91 (s, 3 H), 1.07 (q, J = 7.5 Hz, 2 H), 1.48−1.70 (m, 3 H), 1.75−1.90 (m, 1 H), 3.05−3.15 (m, 2 H), 4.66 (dd, J = 10.3, 3.8 Hz, 1 H), 7.35−7.50 (m, 10 H), 7.55−7.65 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.9 (q), 25.3 (t), 25.6 (t), 32.1 (t), 32.6 (t), 74.6 (d), 128.2 (d), 128.4 (d), 128.9 (d), 129.3 (d), 130.4 (d), 130.5 (d), 131.5 (s), 134.0 (d), 135.3 (d), 135.4 (d), 137.0 (s), 237.7 (s). Anal. Calcd for $C_{25}H_{27}BrO_3SSi$: C, 58.24; H, 5.28. Found: C, 58.10; H, 5.46.

Radical Cyclization of 41. Method (A). 1-(Methyldiphenylsiloxy)cyclohexene (42). To a refluxing mixture of 394 mg (0.763 mmol) of **41** and 642 mg (7.64 mmol) of finely ground sodium bicarbonate in 10.2 mL of benzene was added via syringe pump over 2 h a solution of 0.25 mL 0.916 mmol) of tributyltin hydride and 12.5 mg (0.076 mmol) of AIBN in 5 mL of benzene. The resulting mixture was stirred at 80 °C for another 2 h, filtered, and concentrated in vacuo. The residue was mixed with 0.1 mL of anhydrous triethylamine and chromatographed over silica gel (eluted with hexane) to give 109 mg (88%) of **42** as a colorless liquid: IR (neat) 1670 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.70 (s, 3 H), 1.38−1.50 (m, 2 H), 1.55−1.65 (m, 2 H), 1.87−1.98 (m, 2 H), 1.98−2.05 (m, 2 H), 4.85−4.89 (m, 1 H), 7.30−7.42 (m, 6 H), 7.56−7.63 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −2.5 (q), 22.2 (t), 23.1 (t), 23.8 (t), 29.8 (t), 105.1 (d), 127.8 (d), 129.8 (d), 134.3 (d), 136.3 (s), 150.2 (s). **Method (B).** To a refluxing mixture of 118 mg (0.228 mmol) of **41** and 87.0 μL (0.273 mmol) of allyl(tributyl)-stannane in 3.9 mL of benzene was added via syringe pump over 1 h a solution of 7.0 μL (0.023 mmol) of tributyltin hydride and 3.7 mg (0.023 mmol) of AIBN in 0.7 mL of benzene. The resulting mixture was stirred at 80 °C for another 3 h and concentrated in vacuo, and the residue was chromatographed over silica gel (eluted with hexane) to give 53 mg (79%) of **42**. Further elution with hexane/ethyl acetate (9/1 and then 8/2) gave 34 mg (81%) of allyl phenyl sulfone.[38]

Radical Cyclization of 49. 1-(Methyldiphenylsiloxy)-cyclopentene (50). According to the procedure for the cyclization of **41**, 200 mg (0.399 mmol) of **49** reacted with 0.13 mL (0.48 mmol) of tributyltin hydride, 6.4 mg (0.039 mmol) of AIBN, and 0.503 g (5.98 mmol) of sodium bicarbonate. Purification of the product through silica gel column chromatography (eluted with hexane) gave 59 mg (52%) of **50** as a colorless liquid: IR (neat) 1645 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.75 (s, 3 H), 1.81 (quartet, J = 5.9 Hz, 2 H), 2.16−2.35 (m, 4 H), 4.55−4.62 (m, 1 H, vinyl CH), 7.30−7.50 (m, 6 H, ArH), 7.56−7.70 (m, 4 H, ArH). In another experiment, 2 equiv of decane was added to the reaction mixture as an internal GC standard, and the resulting solution was analyzed by gas chromatography. The yield of **50** determined this way was 99%: t_R = 16.06 min (column temperature = 210 °C, flow rate = 19 mL/min).

Radical Cyclization of 53. 5-Methyl-1-(methyldiphenylsiloxy)cyclopentene (54). Similar as the cyclization of **49**, the cyclization of **53** was analyzed with gas chromatography using tetradecane as internal standard. The yield of **54** was determine as 92%: t_R = 12.40 min (column temperature = 220 °C, flow rate = 18 mL/min). Characteristic ^1H NMR signals of **54**: ($CDCl_3$, 200 MHz) δ 0.70 (s, 3 H), 1.06 (d, J = 7 Hz, 3 H), 2.50−2.62 (m, 1 H), 4.43 (br s, 1 H), 7.30−7.50 (m, 6 H), 7.56−7.70 (m, 4 H).

2-Methyl-5-[1-(methyldiphenylsilyl)-2,6-dithiacyclohexyl]butanol (59). A mixture of 1.43 g (3.57 mmol) of **57** and 162 mg (4.28 mmol) of sodium borohydride in 6 mL of ethanol and 1 mL of dichloromethane was stirred in an ice/water bath for 2 h and then partitioned between ether and water. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed over silica gel (eluted with hexane/ethyl acetate, 8/2) to give 1.26 g (88%) of **59** as a pale yellow oil: IR (neat) 3622, 3482 (br) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.72 (d, J = 6.6 Hz, 3 H), 0.76 (s, 3 H), 1.10−1.28 (m, 1 H), 1.30−1.52 (m, 3 H), 1.81−2.05 (m, 2 H), 2.08−2.30 (m, 2 H), 2.43 (dt, J = 14, 4 Hz, 2 H), 2.98 (br t, J = 14 Hz, 2 H), 3.23−3.30 (m, 2 H), 7.25−7.48 (m, 6 H), 7.79 (d, J = 6 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −3.8, 16.4, 23.9, 24.7, 30.3, 35.0, 36.0, 39.1, 67.7, 127.5, 129.7, 134.2, 135.8; HRMS calcd for $C_{22}H_{30}OS_2Si$ m/z 402.1507, found 402.1507.

5-Bromo-4-methyl-1-(methyldiphenylsilyl)-1-pentanone (60). To a solution of 1.60 g (3.97 mmol) of **59** and 1.58 g (4.77 mmol) of carbon tetrabromide in 4 mL of dichloromethane cooled in an ice/water bath was added over 20 min a solution of 1.24 g (4.77 mmol) of triphenylphosphine in 5 mL of dichloromethane. The reaction mixture was stirred at the same temperature for 2 h and then directly filtered over a short pad of silica gel (eluted with ether). The filtrate was concentrated in vacuo, and the residue was dissolved in 3 mL of dry THF. This THF solution was added to a mixture of 1.72 g (7.95 mmol) of red mercury oxide, 1.72 g of Celite, and 1 mL (7.95 mmol) of borontrifluoride etherate in aqueous THF (H_2O/THF = 3 mL/17 mL). The resulting mixture was stirred at room temperature for 2 h and filtered. The filtrate was partitioned between ether and water. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed over silica gel (eluted with hexane/ethyl acetate, 95/5) to give 0.95 g (63%) of **60** as a yellow oil: IR (neat) 1641 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.76 (s, 3 H), 0.89 (d, J = 7 Hz, 3 H), 1.43 (dq, J = 14, 7 Hz, 1 H), 1.55−1.75 (m, 2 H), 2.66 (t, J = 7 Hz, 2 H), 3.17 (dd, J = 9.5, 6 Hz, 2 H), 3.25 (dd, J = 9.5, 4.5 Hz, 1 H), 7.33−7.50 (m, 6 H), 7.67 (d, J = 7 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.0, 18.5, 27.1, 34.5 40.7, 46.7, 128.2, 130.1, 132.6, 134.9, 243.7; HRMS calcd for $C_{19}H_{23}BrOSi$ m/z 376.0702, found 376.0699.

Radical Cyclization of 62. 4-Methyl-1-(methyldiphenylsiloxy)cyclopentene (30). Similar to the cyclization of **49**, the cyclization of **62** was analyzed with gas chromatography using tetradecane as internal standard. The yield of **30** was determined as 85%: t_R = 10.40 min (column temperature = 220 °C, flow rate = 24 mL/min). Characteristic ^1H NMR signals of **30**: ($CDCl_3$, 300 MHz) δ 0.72 (s, 3 H), 0.98 (d, J = 6 Hz, 3 H), 1.78 (br d, J = 13 Hz, 1 H), 1.89 (br d, J = 13 Hz, 1 H), 2.20−2.50 (m, 3 H), 4.45−4.53 (m, 1 H), 7.35−7.50 (m, 4 H), 7.56−7.70 (m, 4H).

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Supporting Information Available: Characterization data for compounds **9b**,**c**, **10b**,**c**, **11a**,**c**, **12a**,**c**, **14**, **15**, **17**, **23**, **48**, **49**, **52**, **53**, **56**−**58**, **61**, and **62** and copies of ^1H and ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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