Silicon-Directed Decarbonylation of Trans Trimethylsilyl Formyl Octalins[†]

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Abstract: The capability of silicon in directing decarbonylation of aldehydes was investigated. In the presence of 1,2-ethanedithiol and $BF_3 \cdot OEt_2$, *trans*-6-(oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one (**2**) and *trans*-6-(oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one 3-(ethylene dithioacetal) (**4**) were decarbonylated to give *cis*-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one 3-(ethylene dithioacetal) (**7**), *trans*-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one 3-(ethylene dithioacetal) (**8**), and 5-(trimethylsilyl)bicyclo[4.4.0]dec-1(6)-en-3-one 3-(ethylene dithioacetal) (**9**) in a ratio of 14:1.0:4.0 and 12:1.0:2.5, respectively, in total yields of 81–99%. Under the same reaction conditions, *cis*-6-(oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one (**1**) gave a mixture of *cis*-6-(oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one 3-(ethylene dithioacetal) (**3**), *cis*-6-(dimethoxymethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one 3-(ethylene dithioacetal) (**11**), and *cis*-6-(oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one 3,6-bis(ethylene thioacetal) (**12**); no decarbonylation products were formed. Results from ^{13}C NMR spectrometry indicate that the Me_3Si and the formyl groups are nearly trans coplanar in **2** and **4**. Such alignment as well as sulfur atoms at C-3 is necessary for the Me_3Si group to direct the C–CHO bond cleavage.

Silicon-directed carbon–carbon bond cleavages possess synthetic value.[1] We recently developed a new silicon-directed photolytic decarbonylation: the Me_3Si group in aldehydes **1–6**, being either antiplanar with or skewed to the formyl group, directs the photolysis (Scheme I).[2] These reactions involve carboradical intermediates, which are stabilized by a Me_3Si group at the β position.[3,4] We furthermore explored the importance of the alignment of the Me_3Si to the formyl groups in silicon-directed decarbonylation under mild reaction conditions.

Ultraviolet light is very powerful for the cleavage of carbon–carbon bonds. Results from the photolytic decarbonylation, shown in Scheme I, did not reveal a stereoelectronic effect resulting from the Me_3Si group. We considered certain reagents that can induce the decarbonylation of aldehydes under milder conditions than those of photolysis. These reagents include chlorotris(triphenylphosphine)rhodium (Wilkinson's catalyst),[5,6] peroxides,[5,6] tin radicals,[7] and thiol radicals.[8-10] Wilkinson's catalyst cannot decarbonylate hindered aldehydes.[6] Peroxides and tin radicals react with carbon–carbon double bonds[11-14] and with carbon–sulfur bonds.[15] Consequently, we selected 1,2-ethanedithiol.

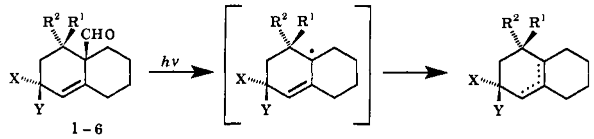
Wierschke,[16] Lambert,[17] and their respective co-workers calculated the acceleration factor contributed by the Me_3Si group in the solvolysis of *cis*- and *trans*-2-(trimethylsilyl)cyclohexyl trifluoroacetates. The trans isomer solvolyzes 10^8 times faster than the cis isomer. The alignment of the Me_3Si–C and the C–O bonds in these trifluoroacetates influences the rate of solvolysis. The Me_3Si–C and the C–O bonds are antiplanar in the trans isomer and skewed in the cis isomer. Similarly, the Me_3Si–C and the C–CHO bonds could be nearly trans coplanar in trans trimethylsilyl enone aldehyde **2**, but skewed in cis trimethylsilyl enone aldehyde **1**. A greater driving force thus would exist in **2** than in **1** for decarbonylation by use of mercaptans because of the favorable bond alignment in **2**.

We report herein an unprecedented silicon-directed decarbonylation. The trans trimethylsilyl aldehydes **2** and **4** reacted with 1,2-ethanedithiol and $BF_3 \cdot OEt_2$ to give decarbonylation products **7–9** in 81% and 99% total yields, respectively (Scheme II). The **7**:**8**:**9** ratio was 14:1.0:4.0 from **2** and 12:1.0:2.5 from **4**. A trans coplanar relationship of the Me_3Si moiety to the formyl group was required for the decarbonylation to occur.

Results

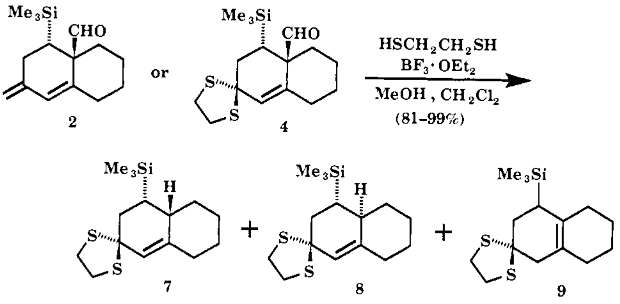
Trimethylsilyl enone aldehydes **1** and **2** are epimers; they possess different configurations at the carbon attached to the Me_3Si group.

Scheme I



1 $R^1 = SiMe_3$; $R^2 = H$; X, Y = O
2 $R^1 = H$; $R^2 = SiMe_3$; X, Y = O
3 $R^1 = SiMe_3$; $R^2 = H$; X, Y = $-SCH_2CH_2S-$
4 $R^1 = H$; $R^2 = SiMe_3$; X, Y = $-SCH_2CH_2S-$
5 $R^1 = SiMe_3$; $R^2 = H$; X = Y = H
6 $R^1 = H$; $R^2 = SiMe_3$; X = Y = H

Scheme II



from **2** 14 (60%) : 1.0 : 4.0
from **4** 12 (77%) : 1.0 : 2.5

Table I. Yields of **4**, **7**, and **10** from the Reaction of **2** with 1,2-Ethanediol and $BF_3 \cdot OEt_2$

equiv		yield, %		
thiol	acid	**4**	**7**	**10**
1.1	3.1	48	32	0
5.9	8.4	0	60	17

Table II. Yields of **3**, **11**, and **12** from the Reaction of **1** with 1,2-Ethanediol and $BF_3 \cdot OEt_2$

equiv		yield, %		
thiol	acid	**3**	**11**	**12**
1.1	3.2	65	22	0
18	45	0	0	99

The C–$SiMe_3$ and the C–CHO bonds in trans isomer **2** are nearly trans coplanar.[2] The Me_3Si group in cis isomer **1** resides at an

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[†] Dedicated to Professor Harry S. Mosher, a creative scientist and devoted educator, on the occasion of his 75th birthday.

[‡] Research fellow of the Alfred P. Sloan Foundation (1986–1990).

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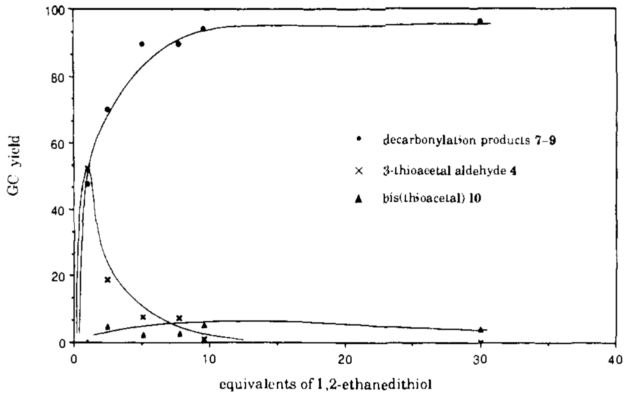
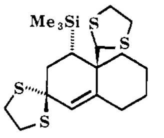


Figure 1. Product distribution for the reaction of *trans*-6-(oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one (**2**) with 40 equiv of $BF_3{\cdot}OEt_2$ and various amounts of 1,2-ethanedithiol.

equatorial position; therefore, the C–$SiMe_3$ bond cannot be coplanar to the C–CHO bond. The rigidity of nuclei in **1** and **2** provides an ideal system for test of the importance of the alignment of the Me_3Si group to the formyl group in the silicon-directed decarbonylation.



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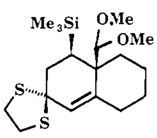

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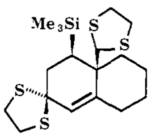

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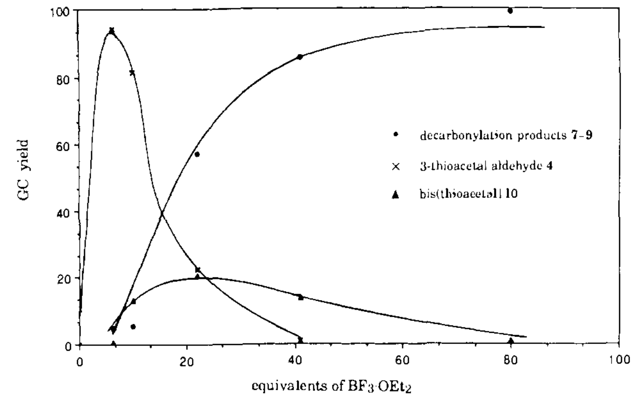
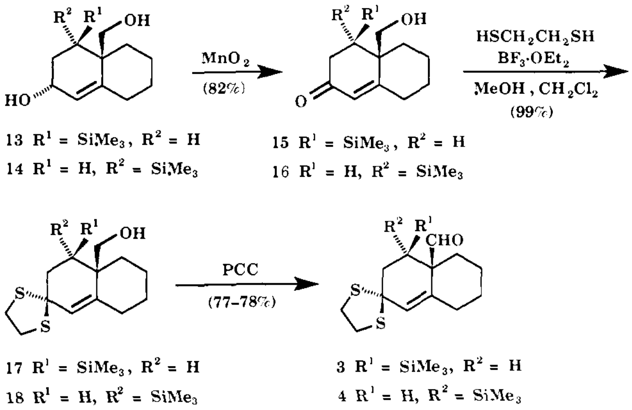


Figure 2. Product distribution for the reaction of *trans*-6-(oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one (**2**) with 25 equiv of 1,2-ethanedithiol and various amounts of $BF_3{\cdot}OEt_2$.

Scheme III



We found that the reaction of trans trimethylsilyl enone aldehyde **2** with various amounts of 1,2-ethanedithiol and $BF_3{\cdot}OEt_2$ gave decarbonylation products **7–9** as well as thioacetals **4** and **10**. In order to understand the decarbonylation, we analyzed the distribution of the major decarbonylation product **7** and the thioacetal products **4** and **10** (Table I). With 1.1 equiv of 1,2-ethanedithiol and 3.1 equiv of $BF_3{\cdot}OEt_2$, we isolated thioacetal aldehyde **4** in 48% yield and decarbonylation product **7** in 32% yield. By increasing the amounts of 1,2-ethanedithiol to 5.9 equiv and $BF_3{\cdot}OEt_2$ to 8.4 equiv, we obtained **7** in 60% yield and bis(thioacetal) **10** in 17% yield. Also, the minor decarbonylation products were detected; the ratio of **7**:**8**:**9** = 14:1.0:4.0.

We did not obtain decarbonylation products from cis trimethylsilyl enone aldehyde **1**. In the presence of 1.1 equiv of 1,2-ethanedithiol and 3.2 equiv of $BF_3{\cdot}OEt_2$, **1** gave thioacetal aldehyde **3** in 65% yield and thioacetal **11** in 22% yield (Table II). With 18 equiv of 1,2-ethanedithiol and 45 equiv of $BF_3{\cdot}OEt_2$, thioacetal **12** was generated in 99% yield.

We also found that 1,2-ethanedithiol, used along with $BF_3{\cdot}OEt_2$ in the decarbonylation of **2**, can be replaced by other mercaptans, such as 1-butanethiol and 1,3-propanedithiol. Similarly, $BF_3{\cdot}OEt_2$ can be substituted by other acids, such as sulfuric acid and tin chloride. Nevertheless, the decarbonylation did not occur when a mercaptan or an acid was used alone.

In a systematic study of the decarbonylation, we varied the concentration of 1,2-ethanedithiol while maintaining the concentrations of trans isomer **2** and $BF_3{\cdot}OEt_2$ (see Figure 1). Likewise, we varied the concentration of $BF_3{\cdot}OEt_2$ while maintaining the concentrations of trans isomer **2** and 1,2-ethanedithiol (see Figure 2). These results indicated that 3-thioacetal aldehyde **4** could be an intermediate in the decarbonylation of **2** to **7–9**. In the presence of $BF_3{\cdot}OEt_2$, 1,2-ethanedithiol is known to add to α,β-unsaturated ketones (thus converting **2** to **4**) preferentially over saturated ketones.[18]

We carried out several control experiments in order to confirm that 3-thioacetal aldehyde **4** was the intermediate for the decarbonylation of aldehyde **2** to **7–9**. Treatment of **2** with 1.2 equiv of 1,2-ethanedithiol and 40 equiv of $BF_3{\cdot}OEt_2$ for 22 h gave a 55%

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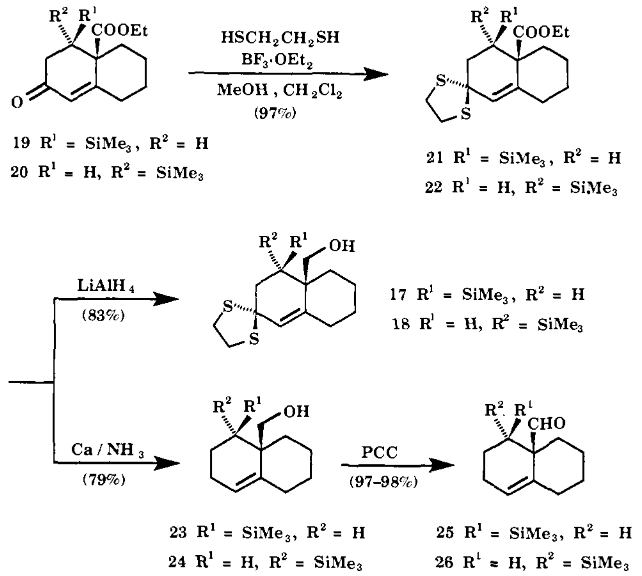
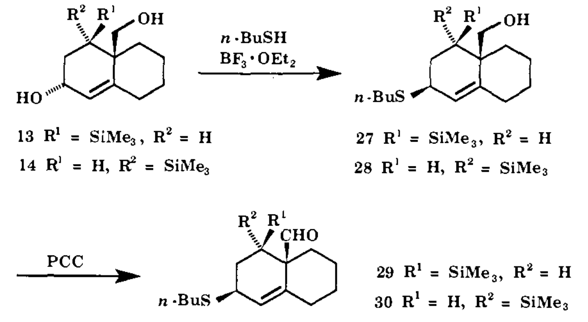
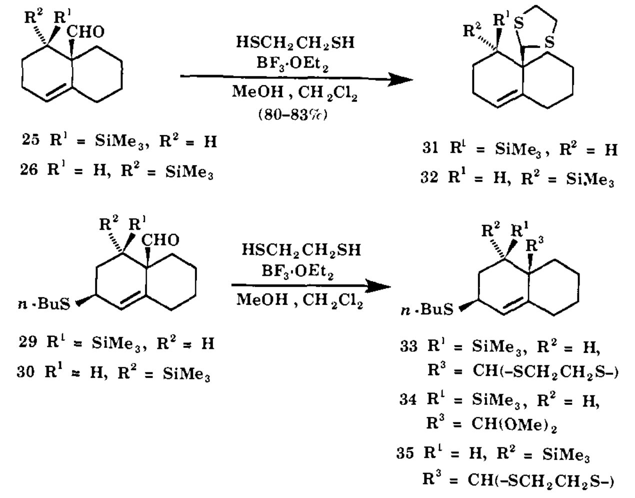
Scheme IV



Scheme V



Scheme VI



yield of aldehyde **4** and a 44% total yield of decarbonylation products **7–9**, as indicated by gas chromatography. The amount of 1,2-ethanedithiol then was increased to 40 equiv and the reaction mixture was stirred for an additional 22 h. We detected **7–9** in 93% total yield and no aldehyde **4**.

In a separate experiment, we treated aldehyde **2** with 41 equiv of 1,2-ethanedithiol and 5.1 equiv of $BF_3{\cdot}OEt_2$ for 23 h. Gas chromatographic analysis showed that a 95% yield of aldehyde **4** and a 3% total yield of decarbonylation products **7–9** were obtained. The amount of $BF_3{\cdot}OEt_2$ then was increased to 36 equiv and the reaction mixture was stirred an additional 22 h. Aldehyde **4** decreased to 9% yield and decarbonylation products **7–9** increased to 80% total yield.

In order to confirm the structure and to have enough of thioacetal aldehydes **3** and **4**, we developed two synthetic pathways. A mixture of trimethylsilyl diols **13** and **14**[2] was oxidized with activated MnO_2 in $CHCl_3$ to give, after separation, enone alcohols **15** in 58% yield and **16** in 24% yield (Scheme III). Treatment of **15** with 2.0 equiv of 1,2-ethanedithiol and 3.0 equiv of $BF_3{\cdot}OEt_2$ afforded thioacetal alcohol **17** in 99% yield. Oxidation of thioacetal alcohol **17** with pyridinium chlorochromate[19] (PCC) in CH_2Cl_2 gave thioacetal aldehyde **3** in 78% yield. Under the same conditions, enone alcohol **16** was converted to thioacetal alcohol **18** (99%), which then was oxidized to thioacetal aldehyde **4** (77%).

Alternatively, thioacetalization of a mixture of trimethylsilyl enone esters **19** and **20**[2] with 1.8 equiv of 1.2-ethanedithiol and 3.0 equiv of $BF_3{\cdot}OEt_2$ generated a mixture of thioacetal esters **21** and **22** in 97% yield (Scheme IV). Reduction of this mixture with $LiAlH_4$, followed by separation, gave the corresponding thioacetal alcohols **17** (43%) and **18** (40%). These compounds were oxidized then with PCC to give thioacetal aldehydes **3** and **4**, respectively, as described above.

We treated thioacetal aldehyde **4** with 43 equiv of 1,2-ethanedithiol and 47 equiv of $BF_3{\cdot}OEt_2$ (Scheme II); similar conditions were used for the decarbonylation of enone aldehyde **2**. The decarbonylation products **7–9** were generated in a ratio of 12:1.0:2.5 in a total yield of 99%. The major product **7** was isolated in 77% yield. As with **2**, both 1,2-ethanedithiol and $BF_3{\cdot}OEt_2$ were required in order to decarbonylate **4**.

To determine the influence of the thioacetal moiety at the C-3 position on the decarbonylation of thioacetal aldehyde **4**, we synthesized trimethylsilyl aldehydes **25** and **26**, as well as trimethylsilyl sulfides **29** and **30**. Aldehydes **25** and **26** do not have the C-3 thioacetal moiety. Sulfide aldehydes **29** and **30**, like thioacetal aldehydes **3** and **4**, possess a C-3 allylic sulfide functionality. Sulfur atoms in **29** and **30**, however, are not close to silicon atoms.

We reduced a mixture of thioacetal esters **21** and **22** with calcium metal[20,21] in refluxing liquid ammonia to give, after separation, alcohols **23** in 32% yield and **24** in 47% yield (Scheme IV). Alcohol **23** was oxidized then with PCC in CH_2Cl_2 to afford aldehyde **25** in 97% yield. Similarly, alcohol **24** was converted to aldehyde **26** in 98% yield.

Scheme V illustrates our preparation of allylic sulfide aldehydes **29** and **30**. Treatment of diol **13** with 4.9 equiv of 1-butanethiol and 6.5 equiv of $BF_3{\cdot}OEt_2$ produced allylic sulfide **27** in 95% yield. Proton NMR spectrometry showed the vinyl proton in **27** had a coupling constant of 5.4 Hz, corresponding to the coupling between vinyl and axial protons. This information led us to assign the *n*-butylthio group to be equatorial; thus the thio group was syn to the angular substituent. Treatment of diol **14** with 8.4 equiv of 1-butanethiol and 9.1 equiv of $BF_3{\cdot}OEt_2$ gave allylic sulfide **28** in only 43% yield. The low yield could be due to the cis relationship between the hydroxyl and the bulky Me_3Si groups; the inherent steric hindrance could retard the substitution process.

Finally, we oxidized sulfide alcohol **27** with PCC in CH_2Cl_2 to afford sulfide aldehyde **29** in 73% yield. Likewise, sulfide alcohol **28** was converted to sulfide aldehyde **30** in 70% yield.

We treated trimethylsilyl aldehydes **25** and **26** separately with 4.2 equiv of 1,2-ethanedithiol and 7.5 equiv of $BF_3{\cdot}OEt_2$ (Scheme VI); similar conditions were used for the decarbonylation of aldehydes **2** and **4**. Unlike **2** and **4**, trans trimethylsilyl aldehyde **26** gave no decarbonylation compounds; only thioacetal **32** (83%) was generated. Cis trimethylsilyl aldehyde **25** also gave thioacetalization product **31** (80%). We then treated allylic sulfide aldehydes **29** and **30** separately with 4.0 equiv of 1,2-ethanedithiol and 6.0 equiv of $BF_3{\cdot}OEt_2$. Again, trans isomer **30** gave no decarbonylation compounds; only thioacetal **35** (69%) was gen-

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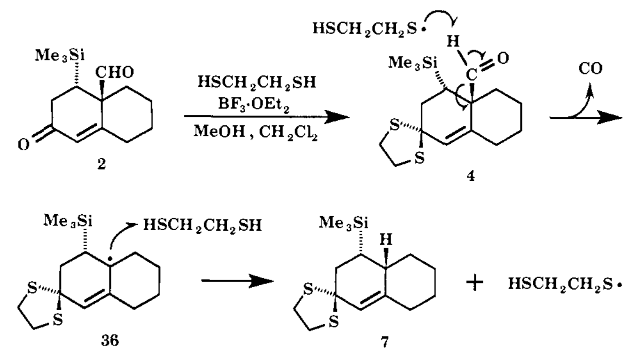
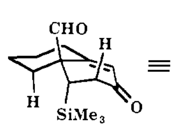
Scheme VII



erated exclusively. Cis isomer **29** led to a mixture of **33** (25%) and **34** (15%).

Axial substituents in cyclohexanes generally cause an upfield NMR shift of carbons in the α position.[22] Previously we found that the carbon attached to the Me$_3$Si group in trans trimethylsilyl isomer **2** (δ 27.07 ppm) is 6.27 ppm upfield of that in cis trimethylsilyl isomer **1** (δ 33.34 ppm).[2] This information supports the suggestion that **2** in CDCl$_3$ has the conformation represented by **2a** and **2b**, instead of **2c**; the Me$_3$Si group in **2** residues in an axial position. We observed the same trend for several other pairs of trimethylsilyl isomers in CDCl$_3$: trans trimethylsilyl aldehyde **4** (δ 27.29 ppm) was 6.57 ppm upfield of cis trimethylsilyl aldehyde **3** (δ 33.86 ppm), trans trimethylsilyl thioacetal **10** (δ 31.50 ppm) 7.71 ppm upfield of cis trimethylsilyl thioacetal **12** (δ 39.21 ppm), trans trimethylsilyl alcohol **14** (δ 25.09 ppm) 9.33 ppm upfield of cis trimethylsilyl alcohol **13** (δ 34.42 ppm), and trans trimethylsilyl alcohol **24** (δ 29.38 ppm) 7.02 ppm upfield of cis trimethylsilyl alcohol **23** (δ 36.40 ppm). For each pair, the carbons attached to the Me$_3$Si groups in trans trimethylsilyl isomers were shifted upfield by 6.5–9.5 ppm. The Me$_3$Si group in these trans trimethylsilyl compounds thus resides in an axial position. Further evidence of the configuration of trimethylsilyl octalins **1–4**, **21–26**, **29**, and **30** was obtained from their electron impact induced fragmentation patterns in mass spectrometry.[23]



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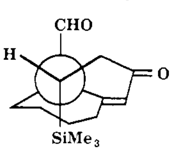
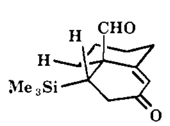




2a 2b 2c

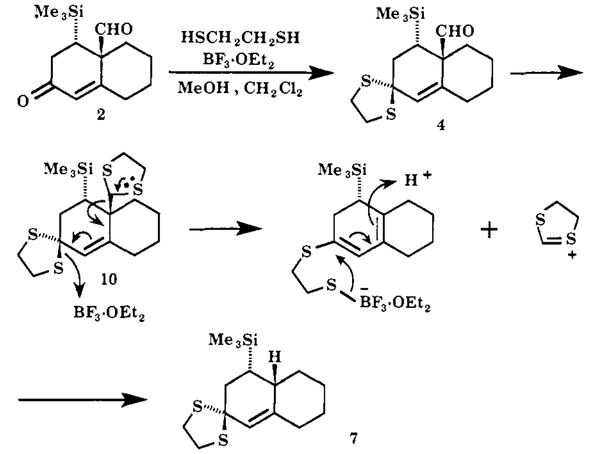
Discussion

Under photolytic conditions, silicon can direct the decarbonylation of cis and trans trimethylsilyl aldehydes **1–6**.[2] On the basis of the mass spectral fragmentation pattern of radical cations of trimethylsilyl aldehydes **1–4**,[23] we envisioned that the Me$_3$Si group would provide the trans isomer **2** with a greater driving force than the cis isomer **1** for decarbonylation.

Under conditions for thioacetalization (involving 1,2-ethanedithiol and BF$_3$·OEt$_2$; see Scheme II), we found that trans isomers **2** and **4** underwent decarbonylation to give **7–9** in 81% and 99% yields, respectively. In contrast, the corresponding cis isomers **1** and **3** did not decarbonylate (Table II). The Me$_3$Si–C and the C–CHO bonds were nearly coplanar in **2** and **4**; however, they were skewed in **1** and **3**. The overlap of the d orbitals of silicon with the developing radical or cationic center would exist in **2** and **4**, but would not in a significant extent in **1** or **3**. Consequently, only aldehydes **2** and **4** underwent the silicon-directed decarbonylation.

The experimental results summarized in Figures 1 and 2 indicate that thioacetal aldehyde **4** is the intermediate in the conversion of **2** to **7**. We also found that the photolytic and the 1,2-ethanedithiol/BF$_3$·OEt$_2$-mediated decarbonylations of aldehyde **4** provided the same products with similar distribution: photolysis gave **7–9** in a ratio of 26:1.0:1.6;[2] use of 1,2-ethanedithiol/BF$_3$·OEt$_2$ gave these products in a ratio of 12:1.0:2.5. These two reactions thus could have the same intermediate (**36**). The Me$_3$Si group in **36** may stabilize the carboradical at the β position.

Scheme VIII



The postulated mechanism shown in Scheme VII would account for the decarbonylation of **2** and **4** to **7**. This pathway, which involves a radical intermediate, is also based on previous work by Waters et al.[8-10] in the decarbonylation of aldehydes with various thiyl radicals.

Homogeneous oxidation of mercaptans by molecular oxygen occurs at room temperature to give the corresponding disulfides.[24-26] Under light, disulfides dissociate readily to give thiyl radicals,[27] which can initiate free-radical reactions.[28] We believe that thiyl radicals, which originate from 1,2-ethanedithiol, could initiate the silicon-directed decarbonylation of trans trimethylsilyl aldehydes **2** and **4**. Lewis acids, such as BF$_3$·OEt$_2$, might catalyze the reaction of 1,2-ethanedithiol with oxygen; thus, increasing the concentration of either 1,2-ethanedithiol or BF$_3$·OEt$_2$ may accelerate this oxidation.

On the other hand, Smith et al.[29] proposed a mechanism involving a cationic intermediate in the decarbonylation of pyrroles with 1,2-ethanedithiol and BF$_3$. By applying Smith's mechanism to our system, we envision that the cationic process shown in Scheme VIII might also be responsible for the conversion of **2** to **7**.

The Me$_3$Si groups in aldehydes **26** and **30** are nearly trans coplanar to formyl groups. Nevertheless, **26** and **30** did not decarbonylate in the presence of 1,2-ethanedithiol and BF$_3$·OEt$_2$ (Scheme VI). Attachment of a second C-3 sulfur atom that is in close proximity to silicon was thus crucial for decarbonylation to occur in **4**.

Conclusion

Trans trimethylsilyl enone aldehyde **2** and trans trimethylsilyl 3-thioacetal aldehyde **4** reacted with 1,2-ethanedithiol and BF$_3$·OEt$_2$ to give decarbonylation products **7–9** in 81% and 99% total yields, respectively. Under similar conditions, the decarbonylation did not occur for the corresponding cis isomers **1** and **3**. For **2** and **4**, the decarbonylation was directed by the Me$_3$Si group, which was nearly trans coplanar to the formyl group. The

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trans coplanarity was crucial for the decarbonylation to proceed.

Experimental Section

General Procedures. All reactions were carried out in oven-dried glassware (120 °C) under an atmosphere of nitrogen unless otherwise indicated. Ethyl acetate and hexanes, from Tilley Chemical Co., were dried and distilled over CaH_2. Boron trifluoride etherate and ethanedithiol, from Aldrich Chemical Co., were dried and distilled over CaH_2. Tetrahydrofuran was dried and distilled from sodium and benzophenone. Chloroform was dried and distilled over CaH_2. Other commercially available chemicals were used directly without purification except where indicated. Calcium, 1-butanethiol, lithium aluminum hydride, manganese(IV) oxide, and pyridinium chlorochromate (PCC) were purchased from Aldrich Chemical Co. Ammonium chloride, CH_2Cl_2, diethyl ether (anhydrous), methanol, and 2-propanol were purchased from J. T. Baker Chemical Co. Melting points were obtained with a Büchi 510 melting point apparatus and are uncorrected. Analytical thin-layer chromatography (TLC) was performed on precoated plates (silica gel GHLF), purchased from Analtech Inc. Visualization of spots on TLC was accomplished by use of UV light and iodine. Mixtures of ethyl acetate and hexanes were used as eluants. Gas chromatographic analyses were performed on a Hewlett-Packard 5794 instrument equipped with a 12.5-m cross-linked methyl silicone gum capillary column (0.2-mm i.d.). The standard conditions for measurement of the retention time (t_R) are as follows. The temperature was 260 °C for the injection port; column temperature program included 70, 120, or 150 °C for the initial temperature, 2.00 min for the duration, 10 °C/min for the increment rate, and 250 °C for the final temperature. Purification by gravity column chromatography was carried out with EM Reagents silica gel 60 (particle size 0.063–0.200 mm, 70–230 mesh ASTM). Separations by radial thin-layer chromatography were performed on a Model 7924T Chromatotron from Harrison Research. The plates (1-, 2-, or 4-mm thickness) were coated with EM Reagents silica gel 60 PF_{254} containing gypsum. Infrared (IR) spectra were measured on a Perkin-Elmer 599B, 710B, or 1600 Fourier transform spectrophotometer. The wavenumbers reported are referenced to the polystyrene 1601-cm^{-1} absorption. Infrared absorption intensities are designated by the following abbreviations: s, strong; m, medium; w, weak; br, broad. Proton NMR spectra were obtained on a Varian CFT-20 (80-MHz) spectrometer or on a Varian XL-400 (400-MHz) spectrometer by use of chloroform-*d* as solvent and internal standard. Carbon-13 NMR spectra were obtained on a Varian XL-400 (100-MHz) spectrometer. Chloroform-*d* was used as solvent. Chemical shifts are referenced to the center of the $CDCl_3$ triplet (δ 77.00). Multiplicities are recorded by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; *J*, coupling constant (hertz). High-resolution mass spectra and electron impact mass spectra (EIMS) were obtained by means of a VG Analytical 70-S mass spectrometer.

Standard Procedure for Thioacetalization. Boron trifluoride etherate was added dropwise to a stirred solution of 1,2-ethanedithiol and a carbonyl compound in CH_2Cl_2 and methanol at 0 °C. This mixture was stirred at room temperature. The reaction then was quenched with saturated aqueous $NaHCO_3$ and the solution was extracted with diethyl ether. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated to give an oil. The oil was pufiried by either gravity column chromatography or radial thin-layer chromatography to afford the pure product(s).

***cis*-6-(Oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one 3-(Ethylene dithioacetal) (3) and *cis*-6-(Dimethoxymethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one 3-(Ethylene dithioacetal) (11).** The standard thioacetalization procedure was followed. Reagents included $BF_3 \cdot OEt_2$ (251 μL, 289 mg, 2.03 mmol, 3.2 equiv), $HSCH_2CH_2SH$ (61 μL, 67 mg, 0.72 mmol, 1.1 equiv), **1** (158.3 mg, 0.632 mmol, 1.0 equiv), CH_2Cl_2 (3.0 mL), and CH_3OH (3.0 mL). The reaction mixture was stirred for 6 h. Purification of the crude products by Chromatotron (2-mm plate, 2.5% EtOAc in hexanes as eluant) gave **3** in 65% yield (134.1 mg, 0.411 mmol) and **11** in 22% yield (51.0 mg, 0.137 mmol) as white solids.

For **3**: mp 120.5–122.0 °C; TLC R_f 0.23 (2.5% EtOAc in hexanes); GC (initial temperature 150 °C) t_R 10.73 min; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.10 (s, 9 H, $Si(CH_3)_3$), 0.85–2.49 (m, 11 H), 3.15–3.43 (m, 4 H, SCH_2CH_2S), 5.92 (t, *J* = 0.9 Hz, 1 H, HC=C), 9.60 (s, 1 H, HCO); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −0.32 (q, SiC_3), 23.73 (t), 27.03 (t), 33.86 (d, SiC), 34.12 (t), 35.93 (t), 39.38 (t), 39.78 (t), 40.38 (t), 54.71 (s, *C*CHO), 66.03 (s, CS_2), 129.49 (d, *C*H=C), 139.41 (s, *C*=CH), 203.60 (d, CHO); IR ($CHCl_3$) 2910 (s, C—H), 2850 (m, C—H), 1720 (s, C=O), 1650 (w, C=C), 1420 (m), 1250 (s, Si—CH_3), 1190 (w), 856 (s), 840 (s), 765 (m), 695 (m) cm^{-1}; EIMS *m/e* (relative intensity) 326 (3), 311 (18), 297 (6), 265 (6), 233 (26), 191 (16), 163 (31), 133 (14), 105 (10), 103 (11), 91 (10), 75 (13), 73 (100), 45 (16); exact mass calcd for $C_{16}H_{26}OS_2Si$ 326.1194, found (70 eV) 326.1196.

For **11**: mp 118.0–119.0 °C; TLC R_f 0.26 (2.5% EtOAc in hexanes; GC (initial temperature 150 °C) t_R 11.50 min; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.04 (s, 9 H, $Si(CH_3)_3$), 0.82–2.31 (m, 11 H), 3.15–3.41 (m, 4 H, SCH_2CH_2S), 3.38 (s, 3 H, OCH_3), 3.44 (s, 3 H, OCH_3), 4.55 (s, 1 H, HCO_2), 5.72 (d, *J* = 0.8 Hz, 1 H, HC=C); IR ($CHCl_3$) 2910 (s, C—H), 1670 (w, C=C), 1440 (m), 1230 (m, Si—CH_3), 1190 (m), 1050 (m), 1020 (m), 970 (m), 910 (m), 850 (s) cm^{-1}; EIMS *m/e* (relative intensity) 372 (9), 237 (6), 191 (4), 175 (3), 163 (4), 131 (3), 104 (4), 91 (3), 89 (8), 75 (100), 73 (21), 59 (6), 45 (4); exact mass calcd for $C_{18}H_{32}O_2S_2Si$ 372.1613, found (70 eV) 372.1624.

Second Method for the Preparation of 3. To a stirred solution of alcohol **17** (975 mg, 2.97 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) was added pyridinium chlorochromate (924 mg, 4.29 mmol, 1.4 equiv). The reaction mixture was stirred for 2.5 h and then diethyl ether (55 mL) was added. The solution was filtered through a pad of Celite, and the black precipitant in the round-bottomed flask was rinsed with diethyl ether (150 mL). The combined filtrates were concentrated and filtered through silica gel with diethyl ether (40 mL) as eluant. Evaporation of the eluant gave an oil. The oil was purified by gravity column chromatography (2.5% EtOAc in hexanes as eluant) to give aldehyde **3** in 78% yield (760.2 mg, 2.33 mmol) as a white solid. The spectroscopic properties of **3** are listed above.

Decarbonylation of *trans*-6-(Oxomethyl)-5-(trimethylsilyl)bicyclo-[4.4.0]dec-1-en-3-one (2). Method 1. Boron trifluoride etherate (251 μL, 289 mg, 2.03 mmol, 3.1 equiv) was added dropwise to a stirred solution of $HSCH_2CH_2SH$ (60.1 μL, 67.4 mg, 0.715 mmol, 1.1 equiv) and enone **2** (165.7 mg, 0.662 mmol, 1.0 equiv) in CH_2Cl_2 (3.0 mL), and CH_3OH (3.0 mL) at 0 °C. The reaction mixture was stirred for 2 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (50 mL) and the solution was extracted with diethyl ether (50 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 50 mL) and brine (50 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated to give an oil. Gas chromatographic analysis of the oil indicated the presence of a mixture of decarbonylation products **7–9** in a ratio of 13:1.0:3.7. Purification of the products by use of Chromatotron (2-mm plate, 2.5% EtOAc in hexanes as eluant) gave **4** in 48% yield (103.7 mg, 0.318 mmol) and **7** in 32% yield (63.7 mg, 0.213 mmol) as white solids.

For **4**: mp 137.5–140.0 °C; TLC R_f 0.22 (2.5% EtOAc in hexanes); GC (initial temperature 150 °C) t_R 10.65 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 1.20–2.35 (m, 11 H), 3.33–3.61 (m, 4 H, SCH_2CH_2S), 5.99 (s, 1 H, HC=C), 9.12 (d, *J* = 1.7 Hz, 1 H, HCO); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −0.82 (q, SiC_3), 22.55 (t), 27.29 (d, SiC), 28.43 (t), 30.75 (t), 34.84 (t), 38.48 (t), 39.58 (t), 40.36 (t), 55.31 (s, *C*CHO), 66.10 (s, CS_2), 129.16 (d, *C*H=C), 139.27 (s, *C*=CH), 201.60 (d, CHO); IR ($CHCl_3$) 2920 (s, C—H), 2840 (m, C—H), 1729 (s, HC=O), 1649 (w, C=C), 1443 (m), 1253 (m, Si—CH_3), 850 (s), 760 (m), 694 (w) cm^{-1}; EIMS *m/e* (relative intensity) 326 (3), 311 (1), 297 (40), 237 (11), 191 (33), 163 (40), 133 (18), 105 (17), 91 (11), 75 (14), 73 (100), 59 (7), 45 (14); exact mass calcd for $C_{16}H_{26}OS_2Si$ 326.1194, found (70 eV) 326.1199.

For **7**: mp 72.5–74.0 °C; TLC R_f 0.27 (1.25% EtOAc in hexanes); GC (initial temperature 150 °C) t_R 9.02 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.04 (s, 9 H, $Si(CH_3)_3$), 1.10–2.31 (m, 12 H), 3.33–3.61 (m, 4 H, SCH_2CH_2S), 5.58 (s, 1 H, HC=C); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −1.49 (q, SiC_3), 27.04 (t), 29.09 (t), 31.14 (d, SiC), 32.20 (t), 36.82 (t), 38.77 (t), 39.03 (d, CH), 39.45 (t), 40.11 (t), 67.24 (s, CS_2), 122.95 (d, *C*H=C), 145.50 (s, *C*=CH); IR ($CHCl_3$) 2930 (s, C—H), 2850 (m, C—H), 1610 (m, C=C), 1500 (s), 1430 (s), 1250 (s, Si—CH_3), 840 (s), 760 (m), 695 (m) cm^{-1}; EIMS *m/e* (relative intensity) 298 (11), 283 (6), 270 (3), 237 (100), 226 (35), 198 (15), 164 (24), 151 (16), 133 (39), 131 (44), 118 (67), 91 (56), 73 (96), 61 (14), 45 (12); exact mass calcd for $C_{15}H_{26}S_2Si$ 298.1245, found (70 eV) 298.1254.

The spectroscopic properties of **8** and **9** are consistent with those reported before.[2]

Method 2. Boron trifluoride etherate (1.40 mL, 1.62 g, 11.4 mmol, 7.2 equiv) was added dropwise to a stirred solution of $HSCH_2CH_2SH$ (671 μL, 752 mg, 7.99 mmol, 5.0 equiv) and enone **2** (399.0 mg, 1.59 mmol, 1.0 equiv) in CH_2Cl_2 (5.0 mL), and CH_3OH (5.0 mL) at 0 °C. The reaction mixture was stirred for 24 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (80 mL) and the solution was extracted with diethyl ether (125 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 80 mL) and brine (80 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated to give an oil. Gas chromatographic analysis of the oil indicated the presence of a mixture of decarbonylation products **7–9** in a ratio of 14:1.0:4.0. The oil was chromatographed on a silica gel column with 2.5% EtOAc in hexanes as eluant to give **7–9** in 81% yield and **10** in 17% yield (109.1 mg, 0.271 mmol) as white solid. Separation of the decarbonylation products **7–9** by use of Chromatotron (2-mm plate, 1.25% EtOAc in hexanes as eluant) gave **7** in 60% yield (286.8 mg, 0.961 mmol) as white solid.

For **10**: mp 133.0–134.0 °C; TLC R_f 0.19 (2.5% EtOAc in hexanes); GC (initial temperature 150 °C) t_R 19.24 min; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.17 (s, 9 H, $Si(CH_3)_3$), 0.82–2.31 (m, 11 H), 3.15–3.43 (m, 8 H, 2 SCH_2CH_2S), 5.24 (s, 1 H, HCS_2), 5.79 (d, J = 0.5 Hz, 1 H, HC=C); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 1.79 (q, SiC_3), 22.26 (t), 27.62 (t), 31.50 (d, SiC), 33.49 (t), 36.35 (t), 38.17 (t), 38.40 (t), 39.69 (t), 40.06 (t), 41.99 (t), 45.49 (s, *C*CHS_2), 62.26 (d, CHS_2), 66.04 (s, CS_2), 128.21 (d, *C*H=C), 144.18 (s, *C*=CH); IR ($CHCl_3$) 2920 (s, C—H), 2850 (m, C—H), 1640 (w, C=C), 1415 (m), 1275 (m, Si—CH_3), 850 (s), 750 (m), 695 (m) cm^{-1}; EIMS m/e (relative intensity) 402 (3), 299 (14), 298 (11), 297 (47), 237 (18), 191 (35), 163 (45), 133 (25), 105 (72), 74 (16), 73 (100), 61 (11), 45 (25); exact mass calcd for $C_{18}H_{30}S_4Si$ 402.1000, found (70 eV) 402.1007.

Decarbonylation of *trans*-6-(Oxomethyl)-5-(trimethylsilyl)bicyclo-[4.4.0]dec-1-en-3-one 3-(Ethylene dithioacetal) (4). Boron trifluoride etherate (80.1 μL, 92.3 mg, 0.651 mmol, 43 equiv) was added dropwise to a stirred solution of $HSCH_2CH_2SH$ (60.1 μL, 67.4 mg, 0.715 mmol, 47 equiv) and aldehyde **4** (5.0 mg, 15.3 μmol, 1.0 equiv) in CH_2Cl_2 (0.25 mL), and CH_3OH (0.25 mL) at 0 °C. The reaction mixture was stirred for 23 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (25 mL) and the solution was extracted with diethyl ether (25 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 25 mL) and brine (25 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated to give an oil. Gas chromatographic analysis of the oil indicated the presence of a mixture of decarbonylation products **7**–**9** in a ratio of 12:1.0:2.5. The oil was chromatographed on a silica gel column with 2.5% EtOAc in hexanes as eluant to give **7**–**9** in 99% yield. Purification of the products by use of Chromatotron (1-mm plate, 1.25% EtOAc in hexanes as eluant) gave **7** in 77% yield (3.5 mg, 11.7 μmol) as a white solid. The spectroscopic properties of **7** are listed above. The spectroscopic properties of **8** and **9** are consistent with those reported before.[2]

Second Method for the Preparation of 4. The procedure for the second method for the preparation of **3**, as aforementioned, was followed. Thus alcohol **18** (423 mg, 1.29 mmol) was converted to aldehyde **4** in 77% yield (324.9 mg, 0.995 mmol) as a white solid. The spectroscopic properties of **4** are listed above.

***cis*-6-(Oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one 3,6-Bis(ethylene dithioacetal) (12).** The standard thioacetalization procedure was followed. Reagents included $BF_3 \cdot OEt_2$ (3.60 mL, 4.15 g, 29.3 mmol, 45 equiv), $HSCH_2CH_2SH$ (1.00 mL, 1.12 g, 11.9 mmol, 18.3 equiv), **1** (163.0 mg, 0.651 mmol, 1.0 equiv), CH_2Cl_2 (10 mL), and CH_3OH (10 mL). The reaction mixture was stirred for 20 h. Purification of the crude product by use of Chromatotron (2-mm plate, 2.5% EtOAc in hexanes as eluant) gave **12** in 99% yield (260.0 mg, 0.646 mmol) as a white solid: mp 142–145 °C; TLC R_f 0.20 (2.5% EtOAc in hexanes); GC (initial temperature 150 °C) t_R 19.36 min; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.18 (s, 9 H, $Si(CH_3)_3$), 0.90–2.51 (m, 11 H), 3.15–3.43 (m, 8 H, 2 SCH_2CH_2S), 5.25 (s, 1 H, HCS_2), 5.66 (d, J = 1.0 Hz, 1 H, HC=C); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 1.35 (q, SiC_3), 22.53 (t), 27.17 (t), 33.38 (t), 37.93 (t), 38.84 (t), 39.00 (t), 39.21 (d, SiC), 40.50 (t), 41.12 (t), 42.41 (t), 44.50 (s, *C*CHS_2), 60.52 (d, CHS_2), 67.18 (s, CS_2), 127.59 (d, *C*H=C), 144.30 (s, C=CH); IR ($CHCl_3$) 2910 (s, C—H), 2850 (m, C—H), 1640 (w, C=C), 1250 (s, Si—CH_3), 850 (s), 770 (m), 690 (m) cm^{-1}; EIMS m/e (relative intensity) 402 (1.1), 298 (11), 297 (44), 191 (33) 163 (44), 133 (23), 105 (56), 73 (100), 61 (13), 45 (14); exact mass calcd for $C_{18}H_{30}S_4Si$ 402.1000, found (70 eV) 402.1026.

***cis*-6-(Hydroxymethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one (15) and *trans*-6-(Hydroxymethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one (16).** Manganese(IV) oxide (activated, black; 9.81 g, 113 mmol, 23 equiv) was added to a solution of diols **13**[2] and **14**[2] (1.25 g, 4.92 mmol, 1.0 equiv) in $CHCl_3$ (120 mL). The solution was stirred for 41 h and filtered. The black precipitate in the flask was rinsed with diethyl ether (200 mL). The combined filtrates were concentrated to a yellow oil. The oil was purified by use of Chromatotron (4-mm plate, 40% EtOAc in hexanes as eluant) to give **15** in 58% yield (726.6 mg, 2.88 mmol) and **16** in 24% yield (295.0 mg, 1.17 mmol) as white solids.

For **15**: mp 99.0–100.5 °C; TLC R_f 0.32 (40% EtOAc in hexanes); GC (initial temperature 150 °C) t_R 8.09 min; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.13 (s, H, $Si(CH_3)_3$), 1.17–2.96 (m, 11 H), 1.53 (br s, 1 H, OH), 3.71–4.02 (m, 2 H, CH_2O), 5.90 (s, 1 H, HC=C); IR (KBr) 3342 (br s, O—H), 2943 (s, C—H), 2861 (m, C—H), 1655 (s, C=O), 1437 (m), 1249 (s, Si—CH_3), 1002 (m), 844 (s), 756 (w), 679 (w) cm^{-1}; exact mass calcd for $C_{14}H_{24}O_2Si$ ($M^{\bullet +} - {}^{\bullet}CH_3$) 237.1311, found (70 eV) 237.1315.

For **16**: mp 99.5–101.0 °C; TLC R_f 0.16 (40% EtOAc in hexanes); GC (initial temperature 150 °C) t_R 7.73 min; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.09 (s, 9 H, $Si(CH_3)_3$), 1.33–2.48 (m, 11 H), 1.59 (br s, 1 H, OH), 3.61 (d, J = 11.3 Hz, 1 H, CH—O), 4.08 (d, J = 11.3 Hz, 1 H, CH—O), 5.91 (s, 1 H, HC=C); IR (KBr) 3448 (br s, O—H), 2943 (s, C—H), 2873 (m, C—H), 1655 (s, C=O), 1455 (m), 1249 (s, Si—CH_3), 1044 (m), 855 (s), 838 (m), 756 (w), 685 (w) cm^{-1}; exact mass calcd for $C_{14}H_{24}O_2Si$ ($M^{\bullet +} - {}^{\bullet}CH_3$) 237.1311, found (70 eV) 237.1312.

***cis*-6-(Hydroxymethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one 3-(Ethylene dithioacetal) (17).** The standard thioacetalization procedure was followed. Reagents included $BF_3 \cdot OEt_2$ (1.20 mL, 1.38 g, 9.76 mmol, 3.1 equiv), $HSCH_2CH_2SH$ (551 μL, 618 mg, 6.56 mmol, 2.1 equiv), enone **15** (788 mg, 3.12 mmol, 1.0 equiv), CH_2Cl_2 (5.0 mL), and CH_3OH (5.0 mL). The reaction mixture was stirred for 2.8 h. Purification of the crude product by gravity column chromatography (10% EtOAc in hexanes as eluant) gave **17** in 99% yield (1.02 g, 3.10 mmol) as a white solid: mp 58.5–60.0 °C; TLC R_f 0.15 (5% EtOAc in hexanes); GC (initial temperature 150 °C) t_R 11.46 min; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 0.85–2.15 (m, 11 H), 1.46 (br s, 1 H, OH), 3.17–3.40 (m, 4 H, SCH_2CH_2S), 3.56 (d, J = 11.3 Hz, 1 H, CH—O), 3.74 (d, J = 11.3 Hz, 1 H, CH—O), 5.70 (s, 1 H, HC=C); IR (CH_2Cl_2) 3400 br s, O—H), 2920 (s, C—H), 2860 (w, C—H), 1720 (m, C=C), 1420 (s), 1250 (s, Si—CH_3), 1300 (s), 950 (s), 870 (s), 830 (s), 765 (m), 695 (m) cm^{-1}; exact mass calcd for $C_{16}H_{28}OS_2Si$ 328.1351, found (70 eV) 328.1355.

***trans*-6-(Hydroxymethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one 3-(Ethylene dithioacetal) (18).** The standard thioacetalization procedure was followed. Reagents included $BF_3 \cdot OEt_2$ (501 μL, 577 mg, 4.07 mmol, 3.0 equiv), $HSCH_2CH_2SH$ (231 μL, 258 mg, 2.74 mmol, 2.0 equiv), enone **16** (345 mg, 1.37 mmol, 1.0 equiv), CH_2Cl_2 (2.5 mL), and CH_3OH (2.5 mL). The reaction mixture was stirred for 2 h. Purification of the crude product by gravity column chromatography (10% EtOAc in hexanes as eluant) gave **18** in 99% yield (445.5 mg, 1.36 mmol) as a white solid: mp 88.0–89.0 °C; TLC R_f 0.14 (10% EtOAc in hexanes); GC (initial temperature 150 °C) t_R 11.39 min; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.10 (s, 9 H, $Si(CH_3)_3$), 0.90–2.20 (m, 11 H), 1.56 (br s, 1 H, OH), 3.24–3.46 (m, 4 H, SCH_2CH_2S), 3.26 (d, J = 10.8 Hz, 1 H, CH—O), 4.09 (dd, J = 10.8, 3.2 Hz, 1 H, CH—O), 5.98 (s, 1 H, HC=C); IR (CH_2Cl_2) 3400 (br s, O—H), 2920 (s, C—H), 2860 (w, C—H), 1720 (w, C=C), 1420 (m), 1250 (s, Si—CH_3), 1030 (m), 950 (m), 870 (s), 830 (s), 765 (m), 695 (m) cm^{-1}; exact mass calcd for $C_{16}H_{28}OS_2Si$ 328.1351, found (70 eV) 328.1352.

Second Method for the Preparation of 17 and 18. Lithium aluminium hydride (219 mg, 5.76 mmol, 4.9 equiv) was added to a stirred solution of a 1.1:1.0 mixture of esters **21** and **22** (438 mg, 1.18 mmol, 1.0 equiv) in anhydrous diethyl ether (30 mL) at 0 °C. The reaction mixture was stirred at room temperature for 17 h. The reaction was quenched at 0 °C with EtOAc (20 mL) and saturated aqueous Na_2SO_4 (5 mL). The resulting white slurry was filtered, washed with EtOAc (100 mL), and refiltered. The combined filtrates were concentrated to give an oil. The oil was purified by use of Chromatotron (2-mm plate, gradient solvent system of 5–20% EtOAc in hexanes as eluant) to afford **17** in 43% yield (166 mg, 0.505 mmol) and **18** in 40% yield (156 mg, 0.476 mmol) as white solids. The spectroscopic properties of **17** and **18** are listed above.

***cis*-6-(Ethoxycarbonyl)-5-(Trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one 3-(Ethylene dithioacetal) (21) and *trans*-6-(Ethoxycarbonyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one 3-(Ethylene dithioacetal) (22).** The standard thioacetalization procedure was followed except that 2-propanol was used as solvent in place of the mixture of CH_2Cl_2 and methanol. Reagents included $BF_3 \cdot OEt_2$ (1.50 mL, 1.73 g, 12.2 mmol, 3.0 equiv), $HSCH_2CH_2SH$ (601 μL, 674 mg, 7.15 mmol, 1.8 equiv), enone esters **19**[2] and **20**[2] (1.194 g, 4.05 mmol, 1.0 equiv), and 2-propanol (20 mL). The reaction mixture was stirred for 24 h. Purification of the crude products by gravity column chromatography (2.5% EtOAc in hexanes as eluant) gave **21** in 53% yield (800 mg, 2.16 mmol) as a colorless oil and **22** in 44% yield (661 mg, 1.78 mmol) as a white solid.

For **21**: TLC R_f 0.20 (2.5% EtOAc in hexanes); GC (initial temperature 70 °C) t_R 19.17 min; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.06 (s, 9 H, $Si(CH_3)_3$), 0.81–2.23 (m, 11 H), 1.27 (t, J = 7.1 Hz, 3 H, CH_3), 3.20–3.51 (m, 4 H, SCH_2CH_2S), 4.15 (q, J = 7.1 Hz, 2 H, OCH_2), 5.74 (d, J = 0.6 Hz, 1 H, HC=C); IR (neat) 2920 (s, C—H), 2850 (m, C—H), 1720 (s, C=O), 1655 (w, C=C), 1440 (m), 1250 (s, Si—CH_3), 1200 (s), 860 (s), 835 (s), 760 (m), 695 (m) cm^{-1}; EIMS m/e (relative intensity) 370 (4), 355 (8), 327 (3), 309 (7), 297 (5), 281 (4), 237 (3), 191 (20), 163 (20), 131 (13), 91 (11), 73 (100), 45 (12); exact mass calcd for $C_{18}H_{30}O_2S_2Si$ (370.1457, found (70 eV) 370.1461.

For **22**: mp 61.0–62.5 °C; TLC R_f 0.18 (2.5% EtOAc in hexanes); GC (initial temperature 70 °C) t_R 19.03 min; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 0.81–2.23 (m, 11 H), 1.27 (t, J = 7.1 Hz, 3 H, CH_3), 3.20–3.51 (m, 4 H, SCH_2CH_2S), 4.12 (dq, J = 11.0, 7.1 Hz, 1 H, OCH), 4.18 (dq, J = 11.0, 7.1 Hz, 1 H, OCH), 5.80 (s, 1 H, HC=C); IR (CH_2Cl_2) 2920 (s, C—H), 2850 (m, C—H), 1720 (s, C=O), 1655 (w, C=C), 1445 (m), 1250 (s, Si—CH_3), 1210 (s), 870 (s), 835 (s), 760 (m), 695 (m), 630 (w) cm^{-1}; EIMS m/e (relative intensity) 370 (4), 355 (4), 309 (6), 297 (21), 281 (4), 237 (9), 191 (51), 163 (30), 133 (16), 105 (7), 75 (10), 73 (100), 45 (13); exact mass calcd for $C_{18}H_{30}O_2S_2Si$ 370.1457, found (70 eV) 370.1468.

***cis*-6-(Hydroxymethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-ene (23) and *trans*-6-(Hydroxymethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-ene (24).** Calcium metal (2.79 g, 69.8 mmol, 26 equiv) was dissolved in liquid ammonia (45 mL) at −78 °C under an atmosphere of argon in a three-necked flask equipped with a Dewar condenser containing dry ice and acetone. To the dark blue solution was added a solution of a mixture of ethylene thioacetals **21** and **22** (987 mg, 2.66 mmol, 1.0 equiv) in THF (20 mL). The cooling bath was removed and the deep blue solution was refluxed for 5.5 h. Solid NH_4Cl and diethyl ether (20 mL) were carefully introduced into the reaction flask and ammonia was allowed to evaporate. Saturated aqueous NH_4Cl was added to the residue, and the aqueuos layer was extracted with two portions of ether. The combined ether solutions were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated to give an orange-pink oil. The oil was purified by use of Chromatotron (4-mm plate, gradient solvent system of 5–10% EtOAc in hexanes as eluant) to afford **23** in 32% yield (202 mg, 0.846 mmol) as a colorless oil and **24** in 47% yield (284 mg, 1.19 mmol) as a white solid.

For **23**: TLC R_f 0.20 (5% EtOAc in hexanes); GC (initial temperature 120 °C) t_R 7.56 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.09 (s, 9 H, $Si(CH_3)_3$), 0.71–2.31 (m, 13 H), 1.52 (br s, 1 H, OH), 3.56 (d, *J* = 11.2 Hz, 1 H, CH—O), 3.87 (d, *J* = 11.2 Hz, 1 H, CH—O), 5.62–5.71 (m, 1 H, HC═C); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −0.03 (q, SiC_3), 22.04 (t), 22.74 (t), 27.04 (t), 27.98 (t), 33.52 (t), 36.40 (d, SiC), 37.30 (t), 42.26 (s, $\mathit{C}CH_2O$), 64.74 (t, CH_2OH), 125.22 (d, *C*H═C), 140.17 (s, *C*═CH); IR (neat) 3350 (br m, O—H), 2910 (s, C—H), 2850 (w, C—H), 1660 (w, C═C), 1445 (w), 1250 (s, Si—CH_3), 1040 (m), 1010 (m), 860 (s), 840 (s), 760 (m), 690 (m), 630 (w) cm^{-1}; EIMS *m/e* (relative intensity) 223 (4), 207 (11), 148 (21), 147 (11), 134 (25), 133 (91), 119 (11), 105 (15), 91 (65), 75 (61), 73 (100), 45 (13); exact mass calcd for $C_{14}H_{26}OSi$ ($M^{\bullet+} - {}^{\bullet}CH_3$) 223.1518, found (70 eV) 223.1521.

For **24**: mp 78.0–80.0 °C; TLC R_f 0.22 (10% EtOAc in hexanes); GC (initial temperature 120 °C) t_R 7.52 min; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.07 (s, 9 H, $Si(CH_3)_3$), 0.95–2.20 (m, 13 H), 1.52 (br s, 1 H, OH), 3.37 (d, *J* = 10.4 Hz, 1 H, CH—O), 3.99 (d, *J* = 10.4 Hz, 1 H, CH—O), 5.75–5.78 (m, 1 H, HC═C); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.19 (q, SiC_3), 21.69 (t) 22.16 (t), 27.01 (t), 28.29 (t), 29.38 (d, SiC), 32.90 (t), 33.94 (t), 44.98 (s, $\mathit{C}CH_2O$), 64.35 (t, CH_2OH), 126.32 (d, *C*H═C), 140.52 (s, *C*═CH); IR (CH_2Cl_2) 3350 (br s, O—H), 2920 (s, C—H); 2840 (m, C—H), 1660 (w, C═C), 1445 (m), 1250 (Si—CH_3) 1040 (m), 860 (s), 840 (s), 760 (m), 690 (m), 630 (w) cm^{-1}; EIMS *m/e* (relative intensity) 238 (0.4), 207 (37), 34 (21), 133 (100), 105 (8), 91 (57), 75 (29), 73 (93), 45 (14); exact mass calcd for $C_{14}H_{26}OSi$ 238.1753, found (70 eV) 238.1755.

***cis*-6-(Oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-ene (25).** To a stirred solution of alcohol **23** (128 mg, 0.536 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) was added pyridinium chlorochromate (186 mg, 0.864 mmol, 1.6 equiv). The reaction mixture was stirred for 5 h and then diethyl ether (80 mL) was added. This solution was washed with saturated aqueous $NaHCO_3$ (3 × 100 mL) and brine (75 mL). The organic layer was separated and dried over anhydrous $MgSO_4$, filtered, and concentrated to give an oil. The oil was purified by use of gravity column chromatography (1.25% EtOAc in hexanes as eluant) to give aldehyde **25** as a colorless oil in 97% yield (124 mg, 0.524 mmol): TLC R_f 0.38 (2.5% EtOAc in hexanes); GC (initial temperature 120 °C) t_R 6.84 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.05 (s, 9 H, $Si(CH_3)_3$, 0.80–2.81 (m, 13 H), 5.74–5.79 (m, 1 H, HC═C), 9.63 (s, 1 H, CHO); IR (neat) 2920 (s, C—H), 2850 (m, C—H), 1720 (s, HC═O), 1670 (w, C═C), 1440 (m), 1255 (s, Si—CH_3), 1020 (w), 860 (s), 845 (s), 770 (m), 690 (m) cm^{-1}; EIMS *m/e* (relative intensity) 236 (9), 221 (11), 207 (7), 146 (23), 145 (11), 133 (67), 131 (16), 118 (11), 91 (65), 75 (32), 73 (100), 59 (11), 45 (16); exact mass calcd for $C_{14}H_{24}OSi$ 236.1596, found (70 eV) 236.1597.

***trans*-6-(Oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-ene (26).** The procedure described above was followed and alcohol **24** (86.5 mg, 0.363 mmol) was oxidized to aldehyde **26** in 98% yield (84.0 mg, 0.353 mmol) as a colorless oil: TLC R_f 0.33 (2.5% EtOAc in hexanes); GC (initial temperature 120 °C) t_R 6.63 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.06 (s, 9 H, $Si(CH_3)_3$), 0.94–2.11 (m, 13 H), 5.76 (tt, *J* = 3.3, 0.4 Hz, 1 H, HC═C), 9.22 (s, 1 H, CHO); IR (neat) 2920 (s, C—H), 2845 (m, C—H), 1700 (s, HC═O), 1655 (w, C═C), 1440 (m), 1240 (s, Si—CH_3), 850 (s), 825 (s), 729 (m), 680 (w) cm^{-1}; EIMS *m/e* (relative intensity) 236 (0.7), 221 (6), 207 (36), 145 (6), 134 (11), 133 (92), 105 (7), 91 (58), 75 (18), 73 (100), 59 (7), 45 (14); exact mass calcd for $C_{14}H_{24}OSi$ 236.1596, found (70 eV) 236.1599.

1-Butyl *r*-3-[*c*-6-(Hydroxymethyl)-*c*-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-enyl] Sulfide (27). Boron trifluoride etherate (601 μL, 692 mg, 4.88 mmol, 6.5 equiv) was added to a stirred solution containing 1-butanethiol (401 μL, 337 mg, 3.73 mmol, 4.9 equiv), diol **13** (192.1 mg, 0.755 mmol, 1.0 equiv), CH_2Cl_2 (5.0 mL), and methanol (6.0 mL) at 0 °C. This mixture was stirred at room temperature in a sealed, round-bottomed flask for 5 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and the solution was extracted with diethyl ether (120 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (100 mL) and brine (100 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated to give an oil. The oil was purified by use of Chromatotron (1-mm plate, 10% EtOAc in hexanes as eluant) to give sulfide **27** as a colorless oil in 95% yield (235.0 mg, 0.719 mmol): TLC R_f 0.32 (10% EtOAc in hexanes); GC (initial temperature 120 °C) t_R 13.43 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.11 (s, 9 H, $Si(CH_3)_3$), 0.86–2.23 (m, 18 H), 1.52 (s, 1 H, OH), 2.30–2.62 (m, 2 H, H_2CS), 3.33–3.44 (m, 1 H, HCS), 3.66 (dd, *J* = 11.3, 1.7 Hz, 1 H, CH—O), 3.85 (d, *J* = 11.3 Hz, 1 H, CH—O), 5.69 (d, *J* = 5.4 Hz, 1 H, HC═C); IR (neat) 3500 (br m, O—H), 2940 (s, C—H), 2855 (m, C—H), 1645 (w, C═C), 1440 (m), 1245 (s, Si—CH_3), 1040 (m), 850 (m), 825 (s), 750 (w) cm^{-1}; exact mass calcd for $C_{18}H_{34}OSSi$ 326.2100, found (70 eV) 326.2105.

1-Butyl *r*-3-[*c*-6-(Hydroxymethyl)-*t*-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-enyl] Sulfide (28). The procedure described above was followed and diol **14** (113 mg, 0.445 mmol) was converted to **28** as a colorless oil in 43% yield (62.8 mg, 0.192 mmol): TLC R_f 0.25 (10% EtOAc in hexanes); GC (initial temperature 120 °C) t_R 13.42 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.07 (s, 9 H, $Si(CH_3)_3$), 0.88–2.19 (m, 18 H), 1,54 (s, 1 H, OH), 2.30–2.59 (m, 2 H, H_2CS), 3.31–3.44 (m, 1 H, HCS), 3.38 (d, *J* = 10.6 Hz, 1 H, CH—O), 3.96 (d, *J* = 10.6 Hz, 1 H, CH—O), 5.77 (d, *J* = 5.7 Hz, 1 H, HC═C); IR (neat) 3420 (br m, O—H), 2960 (s, C—H), 2820 (m, C—H), 1640 (w, C═C), 1425 (m), 1225 (s, Si—CH_3), 1020 (m), 840 (m), 820 (s), 715 (m) cm^{-1}; exact mass calcd for $C_{18}H_{34}OSSi$ 326.2100, found (70 eV) 326.2102.

1-Butyl *r*-3-[*c*-6-(Oxomethyl)-*c*-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-enyl] Sulfide (29). To a stirred solution of alcohol **27** (205 mg, 0.627 mmol, 1.0 equiv) in CH_2Cl_2 (8.0 mL) was added pyridinium chlorochromate (234 mg, 1.09 mmol, 1.7 equiv). The reaction mixture was stirred for 2 h and diethyl ether (100 mL) then was added. This solution was washed with saturated aqueous $NaHCO_3$ (2 × 100 mL) and brine (75 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated to give an oil. The oil was purified by gravity column chromatography (5% EtOAc in hexanes as eluant) to give aldehyde **29** as a colorless oil in 73% yield (149.0 mg, 0.459 mmol): TLC R_f 0.23 (2.5% EtOAc in hexanes); GC (initial temperature 120 °C) t_R 12.77 min; ^1H NMR ($CDCl_3$, 80 MHz), δ 0.10 (s, 9 H, $Si(CH_3)_3$), 0.82–2.12 (m, 18 H), 2.44–2.61 (m, 2 H, H_2CS), 3.36–3.52 (m, 1 H, HCS), 5.81 (dd, *J* = 5.7, 0.8 Hz, 1 H, HC═C), 9.60 (s, 1 H, CHO); IR (neat) 2932 (s, C—H), 2858 (m, C—H), 1719 (s, C═O), 1660 (w, C═C), 1437 (m), 1250 (s, Si—CH_3), 1002 (w), 859 (m), 837 (s), 755 (w), 689 (w) cm^{-1}; EIMS *m/e* (relative intensity) 324 (5), 309 (0.2), 267 (3), 235 (6), 145 (32), 135 (8), 117 (8), 103 (24), 91 (34), 75 (22), 74 (8), 73 (100), 45 (12); exact mass calcd for $C_{18}H_{32}OSSi$ 324.1943, found (70 eV) 324.1945.

1-Butyl *r*-3-[*c*-6-(Oxomethyl)-*t*-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-enyl] Sulfide (30). The procedure described above was followed. After alcohol **28** (59.9 mg, 0.185 mmol) was oxidized, the crude product was purified by gravity column chromatography (2.5% EtOAc in hexanes as eluant) to give aldehyde **30** as a colorless oil in 70% yield (41.9 mg, 0.129 mmol): TLC R_f 0.32 (2.5% EtOAc in hexanes); GC (initial temperature 120 °C) t_R 12.84 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 0.86–2.30 (m, 18 H), 2.41–2.85 (m, 2 H, H_2CS), 3.34–3.50 (m, 1 H, HCS), 5.83 (d, *J* = 5.7 Hz, 1 H, HC═C), 9.13 (d, *J* = 1.2 Hz, 1 H, CHO), IR (neat) 2955 (s, C—H), 2860 (m, C—H), 1726 (s, C═O), 1660 (w, C═C), 1445 (m), 1245 (s, Si—CH_3), 860 (m), 840 (s), 737 (m), 682 (w) cm^{-1}; EIMS *m/e* (relative intensity) 295 (1), 234 (2), 219 (2), 206 (15), 145 (7), 132 (25), 104 (5), 91 (26), 75 (14), 74 (8), 73 (100), 45 (9); exact mass calcd for $C_{18}H_{32}OSSi$ ($M^{\bullet+} - {}^{\bullet}CH_3$) 295.1916, found (70 eV) 295.1918.

***cis*-6-(Oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-ene 6-(Ethylene dithioacetal) (31).** The standard thioacetalization procedure was followed. Reagents included $BF_3{\cdot}OEt_2$ (251 μL, 289 mg, 2.03 mmol, 7.5 equiv), $HSCH_2CH_2SH$ (96.0 μL, 108 mg, 1.14 mmol, 4.2 equiv), **25** (64.0 mg, 0.271 mmol, 1.0 equiv), CH_2Cl_2 (0.50 mL), and CH_3OH (0.50 mL). The reaction mixture was stirred for 22 h. Purification of the crude product by gravity column chromatography (1.25% EtOAc in hexanes as eluant) gave **31** as a colorless oil in 80% yield (68.0 mg, 0.217 mmol): TLC R_f 0.23 (100% hexanes; GC (initial temperature 120 °C) t_R 13.14 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.15 (s, 9 H, $Si(CH_3)_3$), 0.90–2.29 (m, 13 H), 3.15–3.29 (m, 4 H, SCH_2CH_2S), 5.27 (s, 1 H, HCS_2), 5.49–5.53 (m, 1 H, HC═C); IR (neat) 2920 (s, C—H), 2850 (m, C—H), 1735 (w, C═C), 1440 (m), 1255 (Si—CH_3), 860 (s), 840 (s), 790 (w), 760 (w) cm^{-1}; exact mass calcd for $C_{16}H_{28}S_2Si$ ($M^{\bullet+} - {}^{\bullet}CH_3$)

297.1157, found (70 eV) 297.1173.

***trans*-6-(Oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-ene 6-(Ethylene dithioacetal) (32).** The standard thioacetalization procedure was followed. Reagents included $BF_3 \cdot OEt_2$ (501 μL, 577 mg, 4.07 mmol, 18.3 equiv), $HSCH_2CH_2SH$ (201 μL, 225 mg, 2.38 mmol, 10.7 equiv), **26** (52.6 mg, 0.222 mmol, 1.0 equiv), CH_2Cl_2 (1.0 mL), and CH_3OH (1.0 mL). The reaction mixture was stirred for 5.5 h. Purification of the crude product by gravity column chromatography (1.25% EtOAc in hexanes as eluant) gave **32** as a colorless oil in 83% yield (57.4 mg, 0.184 mmol): TLC R_f 0.23 (100% hexanes); GC (initial temperature 120 °C) t_R 13.14 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.10 (s, 9 H, $Si(CH_3)_3$), 0.90–2.30 (m, 13 H), 3.15–3.30 (m, 4 H, SCH_2CH_2S), 5.45 (s, 1 H, HCS_2), 5.54–5.64 (m, 1 H, HC=C); IR (neat) 2920 (s, C—H), 2850 (m, C—H), 1730 (w, C=C), 1440 (m), 1255 ($Si—CH_3$), 860 (s), 840 (s), 790 (w), 760 (w) cm^{-1}; exact mass calcd for $C_{16}H_{28}S_2Si$ ($M^{\bullet +} - {}^{\bullet}CH_3$) 297.1167, found (70 eV) 297.1170.

1-Butyl *r*-3-[*c*-6-(1,3-Dithiolan-2-yl)-*c*-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-enyl] Sulfide (33) and 1-Butyl *r*-3-[*c*-6-(Dimethoxymethyl)-*c*-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-enyl] Sulfide (34). The standard thioacetalization procedure was followed. Reagents included $BF_3 \cdot OEt_2$ (311 μL, 358 mg, 2.52 mmol, 6.1 equiv), $HSCH_2CH_2SH$ (125 μL, 140 mg, 1.49 mmol, 3.6 equiv), aldehyde **29** (133 mg, 0.411 mmol, 1.0 equiv), CH_2Cl_2 (2.0 mL), and CH_3OH (2.0 mL). The reaction mixture was stirred for 19 h. Purification of the crude products by use of the Chromatotron (1-mm plate, 1.25% EtOAc in hexanes as eluant) to give ethylene thioacetal **33** in 25% yield (41.7 mg, 0.104 mmol) and dimethoxymethyl **34** in 15% yield (22.4 mg, 0.060 mmol) as colorless oils. The unreacted aldehyde **29** was recovered in 43% yield (57.7 mg, 0.178 mmol).

For **33**: TLC R_f 0.33 (2.5% EtOAc in hexanes): GC (initial temperature 120 °C) t_R 19.76 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.18 (s, 9 H, $Si(CH_3)_3$), 0.81–2.13 (m, 18 H), 2.43–2.65 (m, 2 H, H_2CS), 3.15–3.25 (m, 4 H, SCH_2CH_2S), 3.25–3.47 (m, 1 H, HCS), 5.26 (s, 1 H, HCS_2), 5.54 (d, J = 4.4 Hz, 1 H, HC=C); IR (neat) 2927 (s, C—H), 2858 (m, C—H), 1654 (w, C=C), 1447 (m), 1377 (w), 1244 (m, $Si—CH_3$), 1079 (m), 1006 (w), 882 (m), 857 (s), 834 (s), 761 (w), 675 (w) cm^{-1}; exact mass calcd for $C_{20}H_{36}S_3Si$ $M^{\bullet +} - {}^{\bullet}CH_3$) 385.1514, found (70 eV) 385.1519.

For **34**: TLC R_f 0.32 (2.5% EtOAc in hexanes); GC (initial temperature 120 °C) t_R 13.67 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.03 (s, 9 H, $Si(CH_3)_3$), 0.80–2.12 (m, 18 H), 2.43–2.65 (m, 2 H, H_2CS), 3.18–3.32 (m, 1 H, HCS), 3.36 (s, 3 H, OCH_3), 3.46 (s, 3 H, OCH_3), 4.56 (s, 1 H, HCO_2), 5.60 (d, J = 4.4 Hz, 1 H, HC=C); IR (neat) 2927 (s, C—H), 2859 (m, C—H), 1657 (m, C=C), 1447 (s), 1244 (s, $Si—CH_3$), 1208 (m), 1187 (w), 1152 (m), 1119 (w), 1108 (m), 1079 (s), 1021 (w), 1006 (w), 958 (w), 882 (m), 853 (s), 833 (s), 750 (w), 677 (w) cm^{-1}; exact mass calcd for $C_{20}H_{38}O_2SSi$ ($M^{\bullet +} - {}^{\bullet}CH_3$) 355.2127, found (70 eV) 355.2132.

1-Butyl *r*-3-[*c*-6-(1,3-Dithiolan-2-yl)-*t*-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-enyl] Sulfide (35). The standard thioacetalization procedure was followed. Reagents included $BF_3 \cdot OEt_2$ (80.1 μL, 92.3 mg, 0.651 mmol, 6.5 equiv), $HSCH_2CH_2SH$ (35.1 mL, 39.3 mg, 0.417 mmol, 4.2 equiv), **30** (32.6 mg, 0.100 mmol, 1.0 equiv), CH_2Cl_2 (0.50 mL), and CH_3OH (0.50 mL). The reaction mixture was stirred for 15 h. Purification of the crude products by gravity column chromatography (2.5% EtOAc in hexanes as eluant) gave ethylene thioacetal **35** in 69% yield (27.6 mg, 0.069 mmol) as a colorless oil. The unreacted aldehyde **30** was recovered in 11% yield (3.7 mg, 0.011 mmol).

For **35**: TLC R_f 0.32 (2.5% EtOAc in hexanes); GC (initial temperature 120 °C t_R 19.34 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.12 (s, 9 H, $Si(CH_3)_3$), 0.86–2.08 (m, 18 H), 2.49–2.67 (m, 2 H, H_2CS), 3.15–3.30 (m, 4 H, SCH_2CH_2S), 3.33–3.53 (m, 1 H, HCS), 5.42 (s, 1 H, HCS_2), 5.53–5.67 (m, 1 H, HC=C); IR (neat) 2927 (s, C—H), 2857 (m, C—H), 1656 (w, C=C), 1450 (m), 1251 (s, $Si—CH_3$), 886 (s) 852 (s), 756 (w), 684 cm^{-1}; exact mass calcd for $C_{20}H_{36}S_3Si$ ($M^{\bullet +} - {}^{\bullet}CH_3$) 385.1514, found (70 eV) 385.1521.

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