X-ray Crystallography. $[(TMT)_2Ru](BF_4)_2\cdot 2CH_3NO_2$. Crystals suitable for the X-ray diffraction study were grown by vapor diffusion of benzene into a nitromethane solution of the complex. A nearly equidimensional cube was cut from a larger crystal. Axial photographs and systematic absences in the data uniquely identified the space group. Corrections for absorption were unnecessary. The structure was solved by a Patterson synthesis and developed from difference maps. The lattice was found to contain two molecules of nitromethane for each [cation]-$[anion]_2$ formula. Both the solvent molecules and the anions were thermally active, leading to a somewhat elevated final *R* factor. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were idealized (d(CH) = 0.96 Å). The BF_4^- atoms were constrained to rigid tetrahedra; a common B–F distance was refined to 1.268 (3) Å, a value somewhat smaller than the usual value of ~1.36 Å. All computations used SHELXTL (5.1) software (Nicolet XRD, Madison, WI). Crystal, data collection, and refinement parameters are listed in Table V. Atomic coordinates and isotropic thermal parameters are listed in Table VI.

$[(TMT)RuCl]_3S(PF_6)$. Crystals suitable for X-ray diffraction were grown by vapor diffusion of diethyl ether into a nitromethane solution of the cluster. A red, translucent platy crystal of dimensions 0.1 × 0.5 × 0.5 mm was cut from a larger crystal. Axial photographs and systematic absences unambiguously defined the space group. Corrections for absorption were applied, with maximum and minimum transmission factors of 0.775 and 0.454, respectively. The structure was solved by direct methods (SHELX-86). The correct Ru atom positions were deduced from an *E* map. Subsequent least-squares-difference Fourier calculations (SHELX-76) revealed positions for the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were idealized. The anisotropic thermal parameters for the fluorine atoms converged to inordinately high values. There was no clear indication of disorder for these positions so the high thermal parameters were retained; consequently, some of the P–F bond lengths converged significantly shorter than expected. Crystal, data collection, and refinement parameters are listed in Table VII. Atomic coordinates and isotropic thermal parameters are listed in Tables VIII.

Acknowledgment. This research was supported by the National Science Foundation. We acknowledge the support of the Petroleum Research Fund, administered by the American Chemical Society. Ruthenium trichloride was obtained on loan from Johnson Matthey. We thank Anton E. Skaugset and Ann E. Ogilvy for gifts of the tetramethylthiophene and for useful discussions.

Supplementary Material Available: Tables of calculated and observed structure factors (28 pages). Ordering information is given on any current masthead page.

Silicon-Directed Decarbonylation of Trimethylsilyl β,γ-Enals by Photolysis

Jih Ru Hwu*,[†] **and Paul S. Furth**

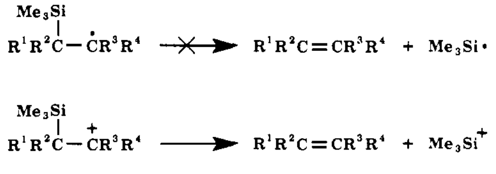
Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218. Received July 8, 1988

Abstract: Irradiation of cis trimethylsilyl aldehyde **9** with UV light generated by a medium-pressure mercury lamp with Pyrex glass filter gave decarbonylated product **11** in 98% yield. Under the same conditions, the corresponding trans trimethylsilyl aldehyde **10** was decarbonylated to afford the same product (**11**) in 89% yield. The trimethylsilyl group directed the fragmentation of the diyls generated from **9** and **10** by preventing oxa-di-π-methane rearrangement and the 1,3 formyl migration. The results indicated that the alkyl radical intermediates, generated by photolysis, can be stabilized by a trimethylsilyl group at the β position; these β-trimethylsilyl alkyl radicals did not eliminate to give alkenes and trimethylsilyl radicals. By use of the stabilizing effect exerted by silicon, photolysis of cis trimethylsilyl aldehyde **33** gave a 98% yield of isomeric trimethylsilyl alkenes **34–36** in a ratio of 10.9:1.0:1.4. Similarly, photolysis of the corresponding trans trimethylsilyl aldehyde **37** afforded a 83% yield of the same products in a ratio of 1.0:25.5:1.6. Furthermore, cis trimethylsilyl aldehyde **38** was photolyzed to produce a 98% yield of isomeric trimethylsilyl alkenes **39–41** in a ratio of 10.9:1.3:1.0; trans trimethylsilyl aldehyde **42** gave a 99% yield of the same trimethylsilyl alkenes in a ratio of 0.1:32.0:1.0. In all of these decarbonylations, the trimethylsilyl group remained in the reaction products.

A Me_3Si group at the β position can stabilize an alkyl radical by ~2.6–2.8 kcal/mol;[1,2] the β-trimethylsilyl alkyl radical normally does not eliminate to give an alkene and $Me_3Si^\bullet$ (Scheme I).[3-5] A Me_3Si group at the β position can stabilize a carbocation by ~38 kcal/mol;[6,7] nevertheless the β-trimethylsilyl carbocation fragments to give an alkene and Me_3Si^+.[8] Although the stabilizing effect of the Me_3Si group has been widely utilized to control reactions with carbocationic intermediates,[8a,9] very few applications involving radicals have been reported.[10] We intended to use the stabilizing ability of the Me_3Si group to direct decarbonylations, which involved radical intermediates.

The decarbonylation of aldehydes occurs in biological systems, such as in the degradation of fatty acids to alkanes via the intermediate octadecanal.[11] Oxidative decarbonylations may be responsible for the conversion of lanosterol to 14-desmethyllanosterol[12] and the transformation of androgens to estrogens.[13]

Scheme I



$$R^1R^2\overset{Me_3Si}{\overset{|}{C}}-\dot{C}R^3R^4 \not\longrightarrow R^1R^2C=CR^3R^4 + Me_3Si^\bullet$$

$$R^1R^2\overset{Me_3Si}{\overset{|}{C}}-\overset{+}{C}R^3R^4 \longrightarrow R^1R^2C=CR^3R^4 + Me_3Si^+$$

The decarbonylation of aldehydes by other chemical means is generally accomplished by use of light,[14] high temperatures,

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

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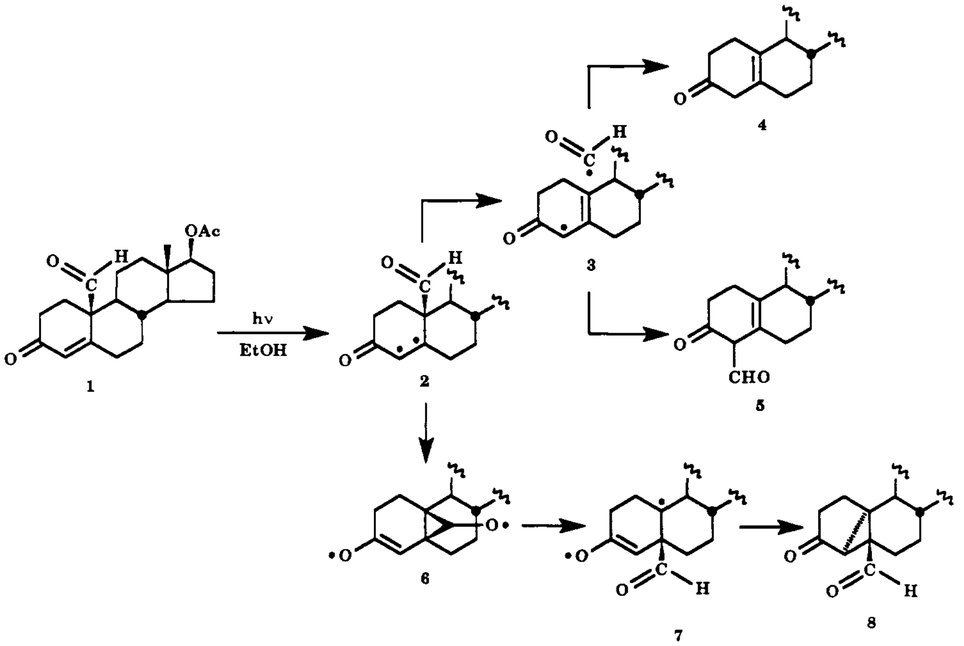
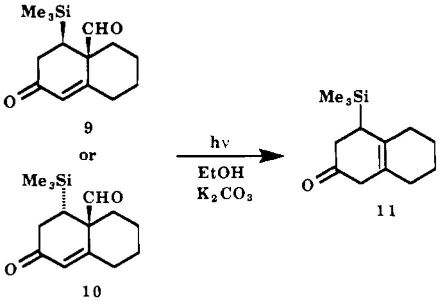
Scheme II

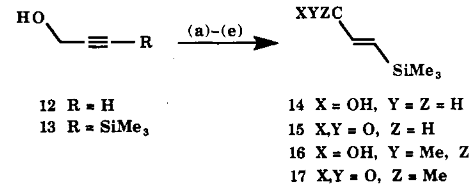


Scheme III



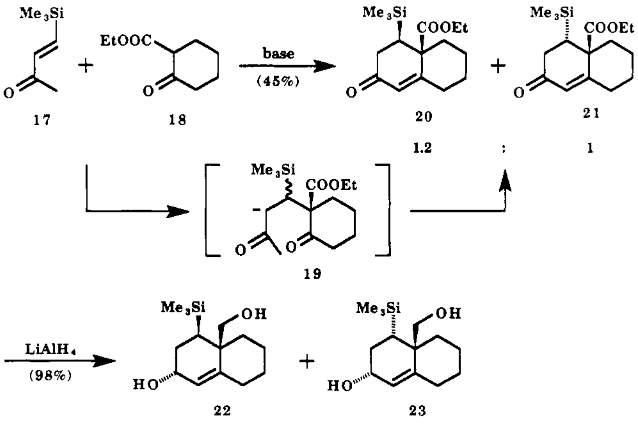
transition metals, metal complexes, or peroxides.[15] The decarbonylation has been utilized in organic synthesis.[16]

Scheme IV[a]



[a] (a) (1) EtMgBr (2.9 equiv), ether; (2) Me$_3$SiCl (2.3 equiv), room temperature; (3) aqueous H_2SO_4; 99%; (b) Red-Al (1.4 equiv), ether; 96%; (c) PCC (1.1 equiv), CH_2Cl_2, room temperature; 85%; (d) MeMgI (2.9 equiv), ether, room temperature; 91%; (e) CrO_3 (1.1 equiv), H_2SO_4, water, acetone, 0 °C; 99%.

Scheme V



Poel, Wehrli, Schaffner, and Jeger reported that photolysis of 17β-acetoxy-19-oxo-4-androsten-3-one (**1**) gave three products (Scheme II):[17] β,γ-enone **4** in 15% yield, formyl enone **5** in 25%

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yield, and β-keto aldehyde **8** in 30% yield. β,γ-Enone **4** comes from the retroformylation of **1**, followed by abstraction of a hydrogen atom from solution. Formyl enone **5** results from a 1,3-shift of the formyl group in cage **3**. β-Keto aldehyde **8** is generated, via intermediates **2**, **6**, and **7**, by an oxa-di-π-methane rearrangement.[14c,18]

We found that the placement of a Me$_3$Si group at an appropriate position in enone aldehydes (i.e., **9** and **10**) dramatically changed the outcome of photolysis: only decarbonylated compound (i.e., **11**) was obtained (Scheme III). The directing effect resulting from silicon was also utilized in the photolytic decarbonylation of other β,γ-enals.

Results and Discussion

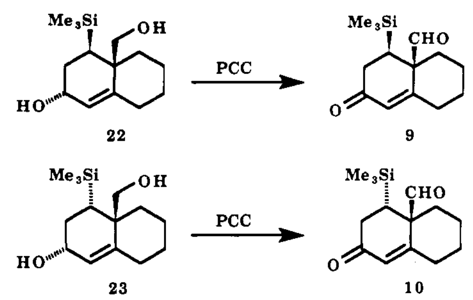
Enone aldehydes **9** and **10** are epimers; the carbons attached to the Me$_3$Si groups have different configurations. The C–SiMe$_3$ and C–CHO bonds in isomer **10** could be trans coplanar. However, the Me$_3$Si group in cis isomer **9** likely resides at an equatorial position; the C–SiMe$_3$ bond then should not be coplanar to the C–CHO bond. These two epimers are ideal substances to test whether the Me$_3$Si group can direct photolysis of enone aldehydes. The results from the photolysis of **9** and **10** will also reveal the importance of the alignment of the Me$_3$Si group to the formyl group.

Synthesis of Cis and Trans Trimethylsilyl Enone Aldehydes 9 and 10. We utilized the Robinson annulation as the key step to construct the skeletons of **9** and **10**. By modifying the procedure developed by Carter, Fleming, and Percival,[19] we obtained trimethylsilyl enone **17** from propargyl alcohol (**12**; Scheme IV). The main difference between the two syntheses is the oxidation of (trimethylsilyl)allyl alcohol **16** to enone **17**. We obtained **17** in 99% yield by using the Jones reagent (CrO$_3$, H$_2$SO$_4$, water, acetone);[20] the protodesilylation of (trimethylsilyl)allyl alcohol **16** and trimethylsilyl enone **17** did not occur under these strong acidic conditions.

We treated trimethylsilyl enone **17** with β-keto ester **18** in the presence of sodium alkoxides to give a mixture of **20** and **21** in 45% overall yield (Scheme V). The ratio of **20** to **21**, determined by GC, was 1.2:1; separation of this mixture by chromatography was not successful. The yield of this reaction was lower than that (75%) of a similar Robinson annulation with *trans*-pent-3-en-2-one and 5-isopropylidene-2-oxocyclohexanecarboxylate, reported by Marshall and Ruden.[21] The lower yield of our annulation may be due to the inefficiency of the Michael addition of sodium enolate of **18** to **17**. The Me$_3$Si group in intermediate **19** could destabilize the β-carbanion[22] and thus increased the steric congestion around the quaternary carbon.

We reduced the mixture of **20** and **21** in anhydrous ether with LiAlH$_4$[23] to give the corresponding diols **22** (54%) and **23** (44%) as the only products. Epimers **20** and **21** were separated by silica gel chromatography. The allylic hydroxyl groups in **20** and **21** were trans to the hydroxymethyl groups;[24] the coupling constants of the C*H*OH methine protons and the CH=C protons were so small that the vinylic protons appeared as a broad peak instead of a doublet. The high stereoselectivity in the reduction of the enone groups in **20** and **21** could result from the coordination of the reducing agent LiAlH$_4$ with the oxygens in the ester groups.[25] A hydride ion of the coordinated LiAlH$_4$ then transferred to the enone carbonyl group from the β face exclusively. In a control experiment, we carried out the reduction under the same conditions as described above except that the reaction was stopped after 4 h. The corresponding allylic alcohols with angular ester groups were isolated in ~20% yield.

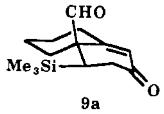
Scheme VI



By treating diol **22** with pyridinium chlorochromate in CH$_2$Cl$_2$,[26] we obtained enone aldehyde **9** (mp 92.0–92.5 °C) in 84% yield (Scheme VI). Under the same conditions, diol **23** was converted to enone aldehyde **10** (mp 58.0–59.0 °C) in 96% yield. Epimers **9** and **10** had the following distinct differences in spectroscopy. The ^{1}H NMR chemical shift of the aldehydic proton in trans isomer **10** (δ 9.35 ppm) was more upfield than that of cis isomer **9** (δ 9.70 ppm). The mass spectrum of **10** possessed a strong peak (65.3% of the relative intensity) related to the fragment resulting from ($M^{\bullet+} - {}^{\bullet}CHO$). The intensity of the peak with the same *m/e* value from **9** was much lower (4.8%).

Nuclear Overhauser Enhancement of the Aldehydic Proton Signals in 9 and 10. The Me$_3$Si group in cis isomer **9** at either the equatorial or the axial position will be near to the formyl group. Therefore, irradiation of the Me$_3$Si protons should give a nuclear Overhauser enhancement[27] greater than 0% for the aldehydic proton. On the contrary, the Me$_3$Si group in trans isomer **10** could be distant with the formyl group by holding an axial position; observation of 0% of the nuclear Overhauser enhancement is possible.

The thermodynamically most stable conformer of cis trimethylsilyl aldehyde **9** should have the Me$_3$Si group at the equatorial position (see **9a** and **9b**). By irradiating the protons in the Me$_3$Si group (δ 0.14 ppm) of **9**, we obtained 19% peak enhancement of the aldehydic proton. Nevertheless, irradiation of the protons in the Me$_3$Si group (δ 0.10 ppm) of **10** did not give any peak increment of the aldehydic proton. These results supported our initial assignment of **9** to be cis and **10** to be trans. We also concluded that the Me$_3$Si group in **10** held an axial position (see **10a** and **10b**).



9a

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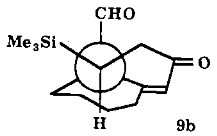
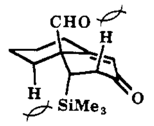
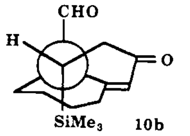


9b

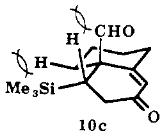


10a

≡



10b



10c

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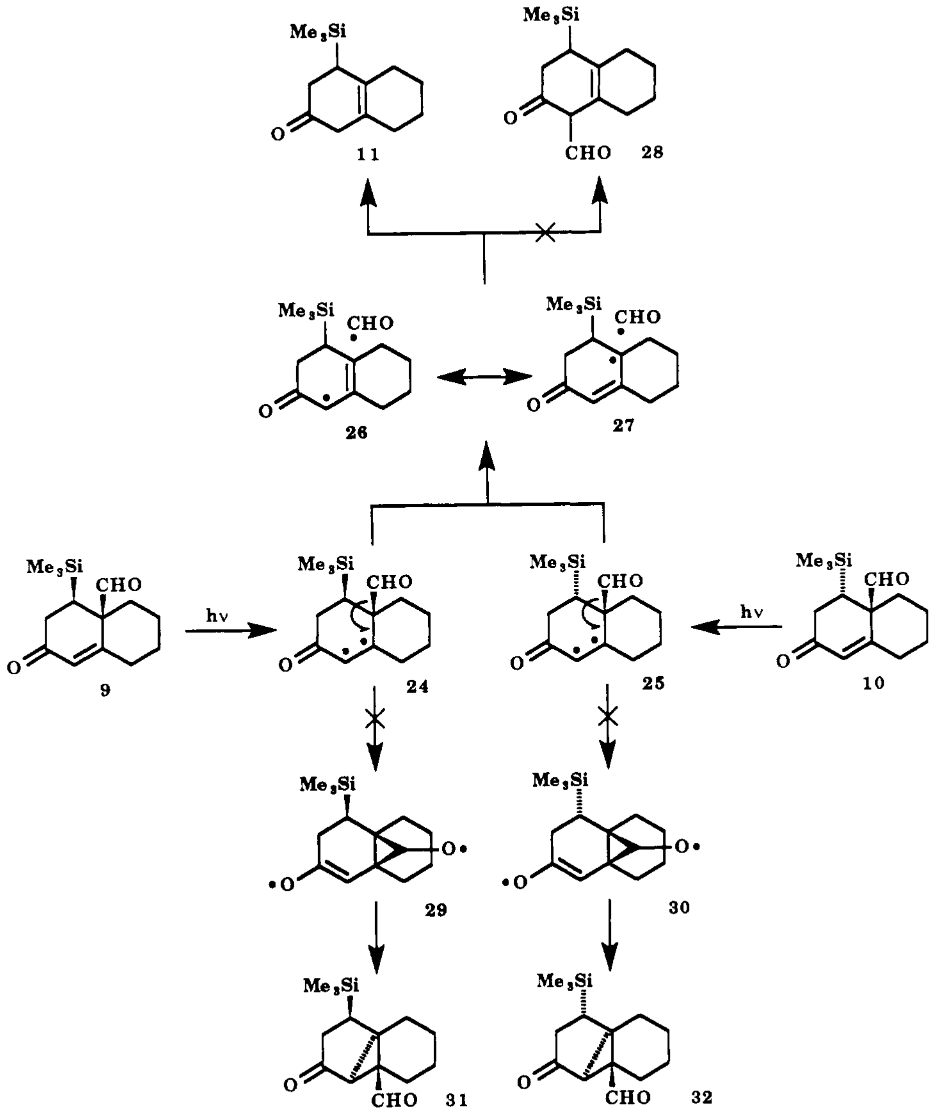
Scheme VII



Axial substituents in cyclohexanes generally cause an upfield shift of the carbons in the α position.[28] Comparing the ^{13}C NMR spectra of **9** and **10** in $CDCl_3$, we found that the carbon attached to the Me_3Si group in **10** (δ 27.07 ppm) was 6.27 ppm more upfield than that in **9** (δ 33.34 ppm). This information further supported the suggestion that trans trimethylsilyl aldehyde **10** in $CDCl_3$ had the conformation represented by **10a** and **10b**: the Me_3Si group being axial.

Our studies by NMR spectroscopy indicated that **10a** was thermodynamically more stable than its conformer **10c**, in which the Me_3Si group located at the equatorial position. Both **10a** and **10c** had a 1,3-interaction between a hydrogen and the Me_3Si group. However, the 1,2-repulsion between a hydrogen and the formyl group in **10c** was more severe than the 1,3-repulsion in **10a**.

Photolysis of Cis and Trans Trimethylsilyl Enone Aldehydes 9 and 10. We photolyzed an ethanol solution of cis enone aldehyde **9** in the presence of K_2CO_3 for 5 h[29] to give trimethylsilyl β,γ-enone **11** in 98% yield (Scheme III). A medium-pressure mercury lamp of 450 W was used as the light source with a Pyrex glass sleeve as light filter. The base K_2CO_3 was utilized to avoid the formation of acetals.[30] In addition, we found that K_2CO_3 was sufficient to keep the reaction matrix in anhydrous conditions, which were essential for obtaining **11** in a high yield.

Under the same photolytic conditions, we obtained **11** from **10** in 89% yield. The Me_3Si group retained in the photolytic product **11**, as indicated by the peak at δ 0.01 ppm (9 H) in its ^1H NMR spectrum. The C–C double bond was not in conjugation with the C=O group: the IR absorptions of C=C and C=O stretching vibrations located at 1672 and 1714 cm^{-1}, respectively. The ^{13}C NMR spectrum of **11** contained 11 peaks, including one quartet at −1.44 ppm for carbons in Me_3Si group, one doublet at 32.02 ppm for the carbon attached to the Me_3Si group, two singlets at 123.21 and 131.57 ppm for the C=C carbons, and one singlet at 212.36 ppm for the C=O carbon.

Background of Stabilization of Alkyl Radicals by β-Silyl Groups. Photolysis of α,β-enone **1**, a compound without a silyl group, gives β,γ-enone **4** as a minor product (15%).[17] However, we found that trimethylsilyl β,γ-enone **11** was the only product in the photolysis of **9** or **10**. We believe that the difference came from the Me_3Si group being capable of stabilizing β-carbon radicals.

In 1969, Jackson reported that the ΔH value for the addition of $Me_3Si^\bullet$ to ethylene was ∼−18 kcal/mol.[31] This radical reaction is essentially irreversible at 140 °C.[3,4] Kira, Sugiyama, and Sakurai also reported that, at high temperatures (130 °C), the spontaneous elimination of $Me_3Si^\bullet$ from the *p*-bis(trimethylsilyl)benzene radical overrides the hydrogen abstraction.[5] However, elimination of $Me_3Si^\bullet$ is not important at low temperature

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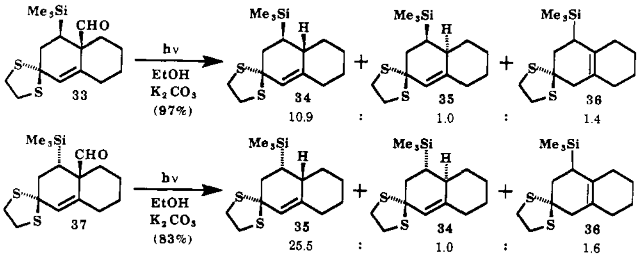
Scheme VIII



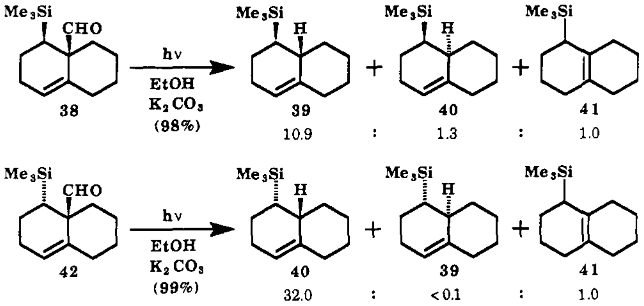
(0 °C). Auner, Walsh, and Westrup estimated the β-stabilization energy resulting from the Me_3Si group in the $Me_3SiCMe_2CH_2^{\bullet}$ radical to be 2.9 ± 1.2 kcal/mol.[1] Davidson, Barton et al. also found that β-silyl substituents might stabilize alkyl radicals by 2.6 ± 1 kcal/mol.[2] The effect of the anchimeric assistance by the Et_3Si group to the formation of $Et_3SiCH_2CH_2^{\bullet}$ radical was utilized by Wilt, Belmonte, and Zieske to abstract a halogen from $Et_3SiCH_2CH_2X$[32] and was employed by Jackson, Ingold, Griller, and Nazran to remove a β-hydrogen atom from Et_4Si.[33] Recently, Conlin et al. reported that the homolytic cleavage of C–C single bonds at high temperatures could be influenced by the β-stabilizing effect of silicon atom.[34]

Mechanism of the Photolytic Decarbonylation of Enone Aldehydes 9 and 10. On the basis of the process shown in Scheme II,[17] we believe that photolysis of enones **9** and **10** afforded the excited species **24** and **25**, respectively. Because alkyl radicals can be stabilized by a Me_3Si group at the β position,[35] **24** and **25** would preferentially give **26** and **27** through the homolytic C–CHO bond fission rather than generate tricyclic, cyclopropyl diradicals **29** and **30**. The trimethylsilyl enone radical species in **26** and **27** was expected to be more stable than the enone radical in **3**. The C–Si σ bond in **26** and **27** could be coplanar to the orbital of the single electron, and therefore, isovalent hyperconjugation[36] may exist. Consequently, the $CHO^{\bullet}$ radical in the cage intermediate, represented by **26** and **27**, had a greater chance to leave and a lesser opportunity to undergo 1,3-shift to give **28**.

A large driving force existed for the cleavage of the C–Si bond in the intermediate represented by **26** and **27** because one of the products would be an arene. Nevertheless, we did not detect any phenol derivative in the photolysis of **9** or **10** at room temperature. Our results supported the finding that β-trimethylsilyl carbon radicals, generated by photolysis, had no tendency to decompose at ambient temperature to give alkenes and $Me_3Si^{\bullet}$.

The trimethylsilyl enone radical species in **26** and **27** finally trapped a hydrogen atom to give trimethylsilyl enone **11** as the only product. We did not obtain any trimethylsilyl α,β-enone. 2-Octalones with the C–C double bond at the fused position are thermodynamically more stable than the conjugated isomers.[37] In addition, the σ–π hyperconjugation between the C=C bond and the C—Si bond in the allylic position could provide **11** with extra stability.[38] A steroid with the same moiety, the trimethylsilyl and the β,γ-enone groups in the A ring, was reported by Minailova, Ivanenko, and Pivnitskii.[39]

Scheme IX



Photolysis of Cis and Trans Trimethylsilyl Enals 33, 37, 38, and 42.[40] In order to show the scope of the silicon-directed decarbonylation, we irradiated other β,γ-enals with different functionalities in the octalin skeleton under the same conditions used for **9** and **10**. Cis trimethylsilyl thioacetal β,γ-enal **33** provided an isomeric mixture of decarbonylated products **34**–**36** in 97% overall yield. The trimethylsilyl group remained in all of these products, which presumably came from a common β-trimethylsilyl alkyl radical intermediate. Analysis of the mixture of gas chromatography (GC) showed that **34**:**35**:**36** ratio was 10.9:1.0:1.4. The major product **34** was isolated in 79% yield. We also obtained the same decarbonylated products in 83% overall yield by irradiating trans trimethylsilyl thioacetal enal **37**. The **35**:**34**:**36** ratio was 25.5:1.0:1.6; the major product **35** was isolated in 75% yield.[41]

Furthermore, we photolyzed cis trimethylsilyl β,γ-enal **38** to give an 98% overall yield of trimethylsilyl alkenes **39**–**41**. The **39**:**40**:**41** ratio was determined as 10.9:1.3:1.0 by GC; the major product **39** was isolated in 80% yield. Photolysis of trans trimethylsilyl β,γ-enal **42** gave the same products in 99% overall yield. The **40**:**39**:**41** ratio was 32.0:0.1:1.0. The trimethylsilyl group again remained in all of the decarbonylated products, which were generated in each of the photochemical reactions.

Driving Force for the Photolytic Decarbonylation. Release of the steric congestion between the Me_3Si and the CHO groups in the cis isomers **9**, **33**, and **38** may offer a driving force for the loss of the formyl group. On the other hand, the Me_3Si group in the trans isomers **10**, **37**, and **42** resided at the axial position; the C–Si and the C–CHO bonds should be near trans coplanar (e.g., see **10b**). Such an alignment could facilitate the cleavage of the C–CHO bond. However, we obtained excellent yields for the photolytic decarbonylation of both the cis and the trans β,γ-enals. This is because UV light is very powerful for the cleavage of the C–CHO bond.[42] Once the common allylic radical (e.g., see **26** and **27**) was generated from either the cis or the trans isomer, the influence of the Me_3Si group on the succeeding reaction (i.e., a hydrogen atom absorption or a 1,3 formyl group migration) will be the same. Our experiments proved that the control of the stereoconfiguration of the Me_3Si group in the starting material was not necessary for the silicon-directed decarbonylation of aldehydes.

Conclusions

Photolysis of trimethylsilyl enals **9**, **10**, **33**, **37**, **38**, and **42** gave the decarbonylated compounds exclusively. The decarbonylation process was directed by the Me_3Si group; the stereoconfiguration of the Me_3Si group in the substrates need not be controlled. The results from the decarbonylation experiments indicated that, under photolytic conditions, a Me_3Si group at the β position was able to stabilize an alkyl radical, and a β-trimethylsilyl alkyl radical did not eliminate to give an alkene and Me_3Si.

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(40) For the preparation and the characterization of these compounds see: Furth, P. S.; Hwu, J. R. *J. Am. Chem. Soc.*, following article in this issue.

(41) The reference compound of thioacetal **36** used in the GC analysis was prepared by treatment of **11** with 1,2-ethanedithiol and $BF_3{\cdot}OEt_2$; see the Experimental Section.

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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 1,2-ethanedithiol from Aldrich were dried and distilled from CaH_2 under reduced pressure. Other commercially available chemicals were used directly without purification except where indicated. Bromoethane, chlorotrimethylsilane, ethanol (anhydrous), ethyl 2-cyclohexanonecarboxylate, iodomethane, lithium aluminum hydride, magnesium turnings, propargyl alcohol, pyridinium chlorochromate, sodium methoxide, and sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al; 3.4 M solution in toluene) were purchased from Aldrich Chemical Co. Acetone, chromium trioxide, dichloromethane, iodine, diethyl ether, potassium carbonate, and 2-propanol were purchased from J. T. Baker Chemical Co. Photolytic experiments were carried out at room temperature by use of a medium-pressure mercury lamp of 450 W from Hanovia. 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 plates was done by use of UV light and iodine. Mixtures of ethyl acetate and hexanes were used as eluants. Gas chromatography 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.). Purification by gravity column chromatography was carried out by use of 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. Medium-pressure liquid chromatography (MPLC) separations[43] were performed at a flow rate of 60 mL/h by use of an ISCO Model 312 metering pump. The columns were packed with EM Reagents silica gel 60 (particle size 0.040–0.063 mm, 230–400 mesh ASTM). Infrared (IR) spectra were measured on a Perkin-Elmer 599B or 710B spectrophotometer. The wavenumbers reported are referenced to the polystyrene 1601-cm^{-1} absorption. Absorption intensities are recorded 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 by use of chloroform-*d* as solvent. Carbon-13 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 with a VG Analytical 70-S mass spectrometer.

3-(Trimethylsilyl)-2-propyn-1-ol (13). Magnesium turnings (10.29 g, 423 mmol, 3.1 equiv) were placed in a dry, three-necked, 1-L, round-bottomed flask equipped with a condenser, a dropping funnel, and a stirring bar. Anhydrous diethyl ether (300 mL) and a crystal of iodine were added into the flask. Bromoethane (42.9 g, 394 mmol, 2.9 equiv) was added dropwise over a 25-min period while the reaction mixture was kept refluxing. After 20 min of stirring, the solution was cooled to 0 °C and propargyl alcohol (**12**; 7.57 g, 135 mmol, 1.0 equiv) in anhydrous diethyl ether (8.0 mL) was added dropwise over a 35-min period. The reaction mixture was warmed to room temperature while stirring continued for 45 min. Chlorotrimethylsilane (33.5 g, 308 mmol, 2.3 equiv) was added into the flask and stirring continued under an atmosphere of nitrogen for 18 h. The reaction was quenched at 0 °C with aqueous H_2SO_4 (3.6 M, 200 mL) and the solution was extracted with diethyl ether (100 mL). The combined organic layers were washed with water (2 × 200 mL) and brine (2 × 150 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated to give alkyne **13** as a yellow oil in 99% yield (17.18 g, 134 mmol). Further purification was unnecessary: TLC R_f 0.20 (10% EtOAc in hexanes); ^1H NMR ($CDCl_3$, 80 MHz) δ 0.18 (s, 9 H, $Si(CH_3)_3$), 1.52 (s, 1 H, OH), 4.27 (s, 2 H, CH_2); IR (neat) 3350 (br s, O—H), 2910 (s, C—H), 2180 (m, C≡C), 1400 (w), 1250 (s, Si—CH_3), 1040 (s), 990 (m), 840 (s), 760 (m), 700 (w), 650 (w) cm^{-1}. The physical and spectroscopic properties of this compound were consistent with those reported in the literature.[19,44–48]

(*E*)-3-(Trimethylsilyl)-2-propen-1-ol (14). Alkyne **13** (17.18 g, 134 mmol, 1.0 equiv) in anhydrous diethyl ether (300 mL) was cooled to 0 °C in a 1-L, round-bottomed flask equipped with a dropping funnel and a stirring bar. Sodium bis(2-methoxyethoxy)aluminum hydride (3.4 M solution in toluene, 55 mL, 187 mmol, 1.4 equiv) in anhydrous diethyl ether (50 mL) was added into the flask over a 25-min period. The solution was warmed to room temperature and stirred for 2 h. The reaction mixture was cooled to 0 °C and quenched by the addition of water (20 mL) and then aqueous H_2SO_4 (3.6 M, 330 mL). The solution was extracted with diethyl ether (100 mL). The combined organic layers were washed with water (300 mL) and brine (150 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated to a yellow oil. This oil was purified by gravity column chromatography (10% EtOAc in hexanes as eluant) to give alkene **14** as a colorless oil in 96% yield (16.93 g, 130 mmol): TLC R_f 0.16 (10% EtOAc in hexanes); ^1H NMR ($CDCl_3$, 80 MHz) δ 0.09 (s, 9 H, $Si(CH_3)_3$), 1.52 (br s, 1 H, OH), 4.22 (dd, *J* = 3.7, 1.1 Hz, 2 H, CH_2), 5.88 (dt, *J* = 18.8, 1.1 Hz, 1 H, CHSi), 6.24 (dt, *J* = 18.8, 3.7 Hz, 1 H, CH=C); IR (neat) 3310 (br s, O—H), 2950 (s, C—H), 1610 (w, C=C), 1400 (w), 1240 (s, Si—CH_3), 1070 (m), 990 (m), 860 (s), 830 (s), 770 (w), 690 (w) cm^{-1}. The physical and spectroscopic properties of this compound were consistent with those reported in the literature.[19,45–49]

(*E*)-3-(Trimethylsilyl)-2-propen-1-al (15). Solid pyridinium chlorochromate (30.3 g, 141 mmol, 1.1 equiv) was added to a stirring solution of alcohol **14** (16.93 g, 130 mmol, 1.0 equiv) in dichloromethane (300 mL). Stirring continued in a sealed flask for 6 h. The solution was filtered through a pad of Celite, and the remaining black precipitant in the flask was rinsed with diethyl ether (200 mL) followed by filtration. The filtrates were combined and washed with saturated aqueous $NaHCO_3$ (4 × 175 mL) and brine (175 mL), dried over $MgSO_4$, and concentrated to give a brown oil. The brown oil was purified by gravity column chromatography (10% EtOAc in hexanes) to give aldehyde **15** as a yellow oil in 85% yield (14.11 g, 110 mmol): TLC R_f 0.51 (10% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 50 °C, duration 2.00 min, increment rate 10 °C/min, final temperature 250 °C) t_R 2.56 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.19 (s, 9 H, $Si(CH_3)_3$), 6.49 (dd, *J* = 18.7, 7.3 Hz, 1 H, CHCO), 7.20 (d, *J* = 18.7 Hz, 1 H, CHSi), 9.51 (d, *J* = 7.3 Hz, 1 H, CHO); IR (neat) 2950 (s, C—H), 1670 (s, C=O), 1240 (s, Si—CH_3), 1080 (s), 990 (m), 860 (s), 830 (s), 770 (w), 720 (m), 690 (w) cm^{-1}. The physical and spectroscopic properties of this compound were consistent with those reported in the literature.[19,47,50]

(*E*)-4-(Trimethylsilyl)-3-buten-2-ol (16). Magnesium turnings (7.72 g, 318 mmol, 2.9 equiv) were placed in a dry, three-necked, 1-L, round-bottomed flask equipped with a condenser, a dropping funnel, and a stirring bar. Anhydrous diethyl ether (240 mL) and a crystal of iodine were added into the flask. Iodomethane (19.8 mL, 45.1 g, 318 mmol, 2.9 equiv) was added dropwise over a 25-min period while the reaction mixture was kept refluxing. After 25 min of stirring, the solution was cooled to 0 °C. A solution of aldehyde **15** (14.11 g, 110 mmol, 1.0 equiv) in anhydrous diethyl ether (4.0 mL) was added into the flask over a 5-min period. The reaction mixture was warmed to room temperature and stirring continued for 45 min under an atmosphere of nitrogen. The solution was cooled to 0 °C; water (25 mL) and aqueous H_2SO_4 (3.6 M, 150 mL) were carefully added into the reaction flask. The solution was extracted with diethyl ether (100 mL). The combined organic layers were washed with brine (2 × 150 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated to give an amber oil. The amber oil was purified by gravity column chromatography (10% EtOAc in hexanes as eluant) to give alcohol **16** as a yellow oil in 91% yield (14.43 g, 100 mmol): TLC R_f 0.22 (10% EtOAc in hexanes); ^1H NMR ($CDCl_3$, 80 MHz) δ 0.07 (s, 9 H, $Si(CH_3)_3$), 1.26 (d, *J* = 6.0 Hz, 3 H, CH_3), 1.52 (br s, 1 H, OH), 4.24 (ddq, *J* = 6.0, 4.3, 0.4 Hz, 1 H, CH—O), 5.79 (dd, *J* = 18.6, 0.4 Hz, 1 H, CHSi), 6.13 (dd, *J* = 18.6, 4.3 Hz, 1 H, CH=C); IR (neat) 3340 (br s, O—H), 2960 (s, C—H), 1610 (w, C=C), 1240 (s, Si—CH_3), 1130 (m), 1060 (m), 990 (m), 940 (m), 870 (s), 830 (s), 770 (w), 740 (w), 695 (w) cm^{-1}. The physical and spectroscopic properties of this compound were consistent with those reported in the literature.[19,51]

(*E*)-4-(Trimethylsilyl)-3-buten-2-one (17). To a stirring solution of alcohol **16** (14.43 g, 100 mmol, 1.0 equiv) in acetone (40 mL) at 0 °C was slowly added Jones reagent (2.77 M CrO_3 solution in 4 M H_2SO_4, 38.0 mL, 105 mmol, 1.1 equiv). After 15 min of stirring at 0 °C in a sealed flask, the reaction mixture was quenched with 2-propanol (16.0

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mL, 12.6 g, 209 mmol, 2.1 equiv). The reaction mixture was diluted with diethyl ether (250 mL) and water (150 mL); the organic layer was separated and washed with water (2 × 100 mL), saturated aqueous $NaHCO_3$ (100 mL), and brine (100 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to give enone **17** as a yellow oil in 99% yield (14.12 g, 99.2 mmol): TLC R_f 0.44 (10% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 50 °C, duration 2.00 min; increment rate 10 °C/min; final temperature 250 °C) t_R 4.00 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.15 (s, 9 H, $Si(CH_3)_3$), 2.27 (s, 3 H, CH_3), 6.43 (d, *J* = 19.3 Hz, 1 H, CH=C), 7.04 (d, *J* = 19.3 Hz, 1 H, CHSi); IR (neat) 2960 (s, C—H), 1665 (s, C=O), 1350 (s), 1240 (s, Si—CH_3), 1210 (m), 1190 (m), 990 (m), 860 (s), 830 (s), 760 (w), 695 (w) cm^{-1}. The physical and spectroscopic properties of this compound were consistent with those reported in the literature.[19,50–54]

Ethyl *cis*-5-(Trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one-6-carboxylate (20) and Ethyl *trans*-5-(Trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one-6-carboxylate (21). Sodium ethoxide in ethanol solution (1.93 M, 7.0 mL, 13.5 mmol, 0.67 equiv) was added slowly to a stirring mixture of ethyl 2-cyclohexanonecarboxylate (**18**; 4.60 g, 27.0 mmol, 1.33 equiv) and enone **17** (2.88 g, 20.2 mmol, 1.00 equiv) at 0 °C. After 5 h, solid sodium methoxide (0.73 g, 14.6 mmol, 0.72 equiv) was added, and the reaction mixture was heated to 83 °C in a preheated oil bath for 40 h. The reaction was quenched with saturated aqueous NH_4Cl (4 mL) and the solution was extracted with diethyl ether (200 mL). The organic layer was washed with aqueous H_2SO_4 (3.6 M, 125 mL), saturated aqueous $NaHCO_3$ (3 × 100 mL), and brine (100 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated to give an amber oil. The amber oil was purified by use of medium-pressure liquid chromatography (25 × 450 mm column, 10% EtOAc in hexanes as eluant) to recover 10% unreacted enone **17** (291.1 mg, 2.05 mmol) and to give a mixture of esters **20** and **21** in a ratio of 1:1.2 as an oil in 45% yield (2.694 g, 9.15 mmol): TLC R_f 0.21 (10% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 50 °C, duration 2.00 min, increment rate 10 °C/min, final temperature 250 °C) **20** t_R 17.86 min, **21** t_R 17.61 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.06 (s, 9 H, $Si(CH_3)_3$), 0.75–2.75 (m, 11 H), 1.27 (t, *J* = 7.1 Hz, 3 H, CH_3), 4.20 (q, *J* = 7.1 Hz, 2 H, CH_2O), 5.92 (s, 1 H, CH=C); IR (neat) 2940 (s, C—H), 2840 (m, C—H), 1720 (s, EtOC=O), 1670 (s, C=O), 1255 (s, Si—CH_3), 1030 (m), 850 (s), 760 (m), 700 (m) cm^{-1}; exact mass calcd for $C_{16}H_{26}O_3Si$ 294.1651, found (70 eV) 294.1658.

***t*-6-(Hydroxymethyl)-*t*-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-*r*-3-ol (22) and *t*-6-(Hydroxymethyl)-*c*-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-*r*-3-ol (23).** Lithium aluminum hydride (1.520 g, 40.1 mmol, 7.7 equiv) was added to a stirring solution of esters **20** and **21** (1.537 g, 5.22 mmol, 1.0 equiv) in anhydrous diethyl ether (100 mL) at 0 °C. The reaction mixture was stirred at room temperature for 18 h. The reaction was quenched at 0 °C with EtOAc (50 mL) and saturated aqueous Na_2SO_4 (20 mL). The resulting slurry was filtered and the precipitate was washed with EtOAc (150 mL) followed by filtration. Concentration of the combined filtrates, followed by purification by Chromatotron (4-mm plate, 40% EtOAc in hexanes as eluant) to give diols **22** in 54% yield (724.0 mg, 2.845 mmol) and **23** in 44% yield (591.2 mg, 2.323 mmol) as white solids.

For **22**: mp 156.0–157.0 °C; TLC R_f 0.28 (40% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 150 °C, duration 2.00 min, increment rate 10 °C/min, final temperature 250 °C) t_R 6.90 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.10 (s, 9 H, $Si(CH_3)_3$), 0.60–2.50 (m, 11 H), 1.52 (s, 2 H, 2 OH), 3.66 (d, *J* = 11.2 Hz, 1 H, CCH—O), 3.90 (d, *J* = 11.2 Hz, 1 H, CCH—O), 3.90–4.20 (m, 1 H, C=C—CH—O), 5.58–5.63 (m, 1 H, CH=C); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −0.15 (q, SiC_3), 22.66 (t), 28.12 (t), 31.81 (t), 33.08 (t), 34.42 (d, SiC), 37.43 (t), 43.44 (s, *C*CH_2OH), 64.27 (t, CH_2OH), 68.86 (d, CHOH), 128.87 (d, *C*H=C), 143.55 (s, *C*=CH); IR (KBr) 3350 (br s, O—H), 2930 (s, C—H), 2850 (m, C—H), 1665 (w, C=C), 1250 (s, Si—CH_3), 1050 (m), 1030 (s), 950 (m), 880 (m), 845 (s), 765 (m), 695 (m) cm^{-1}; EIMS *m/e* (relative intensity) 236 (1.3), 221 (8), 146 (10), 133 (56), 132 (35), 131 (13), 105 (13), 104 (14), 91 (100), 79 (13), 75 (28), 73 (53), 45 (13); exact mass calcd for $C_{14}H_{26}O_2Si$ ($M^{\bullet+} - H_2O$) 236.1596, found (70 eV) 236.1599.

For **23**: mp 182.0–183.0 °C; TLC R_f 0.15 (40% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 150 °C, duration 2.00 min, increment rate 10 °C/min, final temperature 250 °C) t_R 6.73 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.09 (s, 9 H, $Si(CH_3)_3$), 0.60–2.50 (m, 11 H), 1.52 (s, 2 H, 2 OH), 3.29 (d, *J* = 10.5 Hz, 1 H, CCH—O), 3.90–4.18 (m, 1 H, C=C—CH—O), 4.09 (d, *J* = 10.5 Hz, 1 H, CCH—O), 5.71–5.75 (m, 1 H, CH=C); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −0.14 (q, SiC_3), 21.98 (t), 25.09 (d, SiC), 28.09 (t), 31.76 (t), 32.49 (t), 33.76 (t), 45.23 (s, *C*CH_2OH), 64.72 (t, CH_2OH), 68.78 (d, CHOH), 130.99 (d, *C*H=C), 142.71 (s, *C*=CH); IR (KBr) 3350 (br s, O—H), 2930 (s, C—H), 2850 (m, C—H), 1670 (w, C=C), 1250 (s, Si—CH_3), 1050 (m), 1030 (s), 1000 (m), 950 (m), 880 (m), 845 (s), 765 (m), 695 (m) cm^{-1}; EIMS *m/e* (relative intensity) 239 (0.2), 223 (4), 149 (6), 134 (13), 133 (67), 107 (9), 105 (11), 92 (15), 91 (100), 75 (48), 73 (48), 55 (11), 45 (13); exact mass calcd for $C_{14}H_{26}O_2Si$ ($M^{\bullet+} - {}^{\bullet}CH_3$) 239.1467, found (70 eV) 239.1469.

***trans*-6-(Oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one (10).** To a stirring solution of diol **23** (210.0 mg, 0.825 mmol, 1.0 equiv) in dichloromethane (10 mL) was added pyridinium chlorochromate (509.6 mg, 2.36 mmol, 2.9 equiv). After 5 h of stirring, diethyl ether (70 mL) was added. The solution was filtered through a pad of Celite, and the black precipitant in the flask was rinsed with diethyl ether (70 mL) followed by filtration. The combined filtrates were concentrated and filtered through silica gel with diethyl ether (25 mL) as eluant. Purification of the crude product by use of Chromatotron (2-mm plate, 10% EtOAc in hexanes as eluant) to give aldehyde **10** as a white solid in 96% yield (200.4 mg, 0.800 mmol): mp 58.0–59.0 °C; TLC R_f 0.15 (10% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 150 °C, duration 2.00 min, increment rate 10 °C/min, final temperature 250 °C) t_R 6.35 min; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.10 (s, 9 H, $Si(CH_3)_3$), 1.35–2.45 (m, 11 H), 6.03 (d, *J* = 0.8 Hz, 1 H, CH=C), 9.35 (s, 1 H, CHO); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.13 (q, SiC_3), 22.80 (t), 27.07 (d, SiC), 27.17 (t), 32.14 (t), 34.62 (t), 35.63 (t), 56.54 (s, *C*CHO), 127.30 (d, *C*H=C), 161.39 (s, *C*=CH), 198.09 (s, CO), 200.23 (d, CHO); IR ($CHCl_3$) 2935 (s, C—H), 2850 (m, C—H), 1720 (s, CH=O), 1670 (s, C=O), 1255 (s, Si—CH_3), 850 (s), 770 (m), 695 (m) cm^{-1}; EIMS *m/e* (relative intensity) 235 (4), 222 (15), 221 (65), 205 (20), 180 (11), 179 (26), 132 (5), 118 (7), 91 (11), 75 (20), 73 (100), 45 (28), 43 (10); exact mass calcd for $C_{14}H_{22}O_2Si$ ($M^{\bullet+} - {}^{\bullet}CH_3$) 235.1154, found (70 eV) 235.1158.

***cis*-6-(Oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one (9).** To a stirring solution of diol **22** (487.5 mg, 1.92 mmol, 1.0 equiv) in dichloromethane (20 mL) was added pyridinium chlorochromate (940.7 mg, 4.36 mmol, 2.3 equiv). After 3.5 h of stirring, diethyl ether (80 mL) was added. The solution was filtered through a pad of Celite, and the black precipitant in the flask was rinsed with diethyl ether (100 mL) followed by filtration. The combined filtrates were concentrated and filtered through silica gel with diethyl ether (25 mL) as eluant. Purification of the crude product by use of Chromatotron (2-mm plate, 10% EtOAc in hexanes as eluant) to give aldehyde **9** as a white solid in 84% yield (404.4 mg, 1.62 mmol): mp 92.0–92.5 °C: TLC R_f 0.15 (10% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 150 °C, duration 2.00 min, increment rate 10 °C/min, final temperature 250 °C) t_R 6.68 min; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.14 (s, 9 H, $Si(CH_3)_3$), 1.31–2.62 (m, 11 H), 6.05 (d, *J* = 1.3 Hz, 1 H, CH=C), 9.70 (s, 1 H, CHO); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −0.01 (q, SiC_3), 23.80 (t), 26.43 (t), 33.34 (d, SiC), 34.80 (t), 35.77 (t), 36.19 (t), 56.92 (s, *C*CHO), 127.38 (d, *C*H=C), 162.79 (s, *C*=CH), 198.41 (s, CO), 201.02 (d, CHO); IR ($CHCl_3$) 2930 (s, C—H), 2850 (m, C—H), 1720 (s, CH=O), 1670 (s, C=O), 1255 (s, Si—CH_3), 850 (s), 765 (m), 700 (m) cm^{-1}; EIMS *m/e* (relative intensity) 235 (9), 221 (5), 217 (6), 205 (5), 179 (8), 132 (14), 118 (17), 91 (11), 75 (26), 73 (100), 55 (7), 45 (17), 41 (9); exact mass calcd for $C_{14}H_{22}O_2Si$ ($M^{\bullet+} - {}^{\bullet}CH_3$) 235.1154, found (70 eV) 235.1155.

5-(Trimethylsilyl)bicyclo[4.4.0]dec-1(6)-en-3-one (11). Method 1. A solution of aldehyde **9** (67.5 mg, 0.270 mmol, 1.0 equiv) in anhydrous ethanol (8.0 mL) over anhydrous, granular potassium carbonate (95.1 mg) was sealed in a 10-mm NMR tube. This solution was irradiated for 5 h with UV light that was filtered through a Pyrex glass sleeve. The solution was decanted into a round-bottomed flask with diethyl ether (5 mL) and concentrated to a reddish oil. This oil was purified by gravity column chromatography (5% EtOAc in hexanes as eluant) to give **11** as a colorless oil in 89% yield (53.7 mg, 0.241 mmol).

Method 2. The above procedure was followed except that **9** was replaced by aldehyde **10** (66.3 mg, 0.265 mmol, 1.0 equiv) and 58.6 mg of anhydrous, granular potassium carbonate was used. After the reaction mixture was concentrated to give an amber-orange oil, the product was purified by gravity column chromatography (5% EtOAc in hexanes as eluant) to give **11** as a colorless oil in 98% yield (57.9 mg, 0.260 mmol).

For **11**: TLC R_f 0.43 (10% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 110 °C, duration 2.00 min, increment rate 10 °C/min, final temperature 250 °C) t_R 7.13 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.01 (s, 9 H, $Si(CH_3)_3$), 1.09–2.20 (m, 9 H), 2.25–2.75 (m, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −1.44 (q, SiC_3), 22.73 (t), 23.28 (t), 29.90 (t), 31.17 (t), 32.02 (d, SiC), 41.55 (t), 44.65 (t), 123.21 (s), 131.57 (s), 212.36 (s, CO); IR (neat)

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2931 (s, C—H), 2855 (m, C—H), 1714 (s, C=O), 1672 (w, C=C), 1249 (m, Si—CH_3), 850 (s), 757 (w), 690 (w) cm^{-1}; exact mass calcd for $C_{13}H_{22}OSi$ 222.1440, found (70 eV) 222.1442.

Photolysis of *cis*-6-(Oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one 3-(Ethylene dithioacetal) (33). A solution of aldehyde **33** (15.8 mg, 48.4 μmol, 1.0 equiv) in anhydrous ethanol (8.0 mL) over anhydrous, granular potassium carbonate (114 mg) was sealed in a 10-mm NMR tube. This solution was irradiated for 20 h with UV light that was filtered through a Pyrex glass sleeve. The solution was decanted into a round-bottomed flask with diethyl ether (5 mL) and concentrated to give a mixture of alkenes **34–36** as an orange oil in 99% yield (14.4 mg, 48.2 μmol). Results from GC analysis indicated that **34–36** were present in a ratio of 10.9:1.0:1.4. The mixture was separated by gravity column chromatography (1.25% EtOAc in hexanes as eluant) to give **34** as a white solid in 79% yield (11.4 mg, 38.2 μmol).

For **34**: mp 63.5–65.0 °C; TLC R_f 0.25 (1.25% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 150 °C, duration 2.00 min, increment rate 10 °C/min, final temperature 250 °C) t_R 8.83 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 1.11–2.38 (m, 12 H), 3.23–3.46 (m, 4 H, SCH_2CH_2S), 5.64 (s, 1 H, *H*C=C); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −1.59 (q, SiC_3), 26.48 (t), 27.62 (t), 28.41 (d, SiC), 35.69 (t), 36.05 (t), 38.14 (d, CH), 39.54 (t), 39.99 (t), 42.24 (t), 66.51 (s, CS_2), 124.67 (d, *C*H=C), 143.92 (s, *C*=CH); IR (CH_2Cl_2) 2930 (s, C—H), 2850 (m, C—H), 1650 (m, C=C), 1440 (s), 1250 (s, Si—CH_3), 850 (s), 760 (m), 690 (m) cm^{-1}; exact mass calcd for $C_{15}H_{26}S_2Si$ 298.1245, found (70 eV) 298.1253.

The physical and spectroscopic properties of alkenes **35** and **36** are listed below.

Photolysis of *trans*-6-(Oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]-dec-1-en-3-one 3-(Ethylene dithioacetal) (37). A solution of aldehyde **37** (16.3 mg, 49.9 μmol, 1.0 equiv) in anhydrous ethanol (8.0 mL) over anhydrous, granular potassium carbonate (86 mg) was sealed in a 10-mm NMR tube. This solution was irradiated for 20 h with UV light that was filtered through a Pyrex glass sleeve. The solution was decanted into a round-bottomed flask with diethyl ether (5 mL) and concentrated to give a mixture of alkenes **34–36** as an orange oil in 83% yield (12.4 mg, 41.5 μmol). Results from GC analysis indicated that **34–36** were present in a ratio of 1.0:25.5:1.6. The mixture was separated by gravity column chromatography (1.25% EtOAc in hexanes as eluant) to give **35** as a white solid in 75% yield (11.2 mg, 37.5 μmol).

For **35**: mp 72.5–74.0 °C; TLC R_f 0.27 (1.25% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 150 °C, duration 2.00 min, increment rate 10 °C/min, final temperature 250 °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 physical and spectroscopic properties of alkene **34** are listed above, and those for alkene **36** below.

5-(Trimethylsilyl)bicyclo[4.4.0]dec-1(6)-en-3-one 3-(Ethylene dithioacetal) (36). Boron trifluoride etherate (250 μL, 289 mg, 2.03 mmol, 10.6 equiv) was added dropwise to a stirring solution of 1,2-ethanedithiol (95.0 μL, 107 mg, 1.13 mmol, 5.3 equiv) and ketone **11** (42.8 mg, 0.192 mmol, 1.0 equiv) in dichloromethane (0.50 mL) and methanol (0.50 mL) at 0 °C. This solution was stirred at room temperature in a sealed flask for 20 h. The reaction was quenched with saturated aqueous $NaHCO_3$. The resulting solution was extracted with diethyl ether. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated to give an oil. This oil was purified by gravity column chromatography (1.25% EtOAc in hexanes as eluant) to give ethylene thioacetal **37** as a colorless oil in 53% yield (29.9 mg, 0.100 mmol): TLC R_f 0.24 (1.25% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 150 °C, duration 2.00 min, increment rate 10 °C/min, final temperature 250 °C) t_R 8.71 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.06 (s, 9 H, $Si(CH_3)_3$), 1.30–2.38 (m, 13 H), 3.20–3.32 (m, 4 H, SCH_2CH_2S); IR (neat) 2924 (s, C—H), 2855 (m, C—H), 1720 (w, C=C), 1434 (m), 1275 (m), 1248 (s, Si—CH_3), 896 (s), 837 (m), 758 (w), 686 (w) cm^{-1}; exact mass calcd for $C_{15}H_{26}S_2Si$ 298.1245, found (70 eV) 298.1251.

Photolysis of *cis*-6-(Oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-ene (38). A solution of aldehyde **38** (150.6 mg, 0.637 mmol, 1.0 equiv) in anhydrous ethanol (16.0 mL) over anhydrous, granular potassium carbonate (369 mg) was sealed in two 10-mm NMR tubes. This solution was irradiated for 21 h with UV light that was filtered through a Pyrex glass sleeve. The solution was decanted into a round-bottomed flask with diethyl ether (5 mL) and concentrated to give a mixture of alkenes **39–41** as an oil in 98% yield (130.6 mg, 0.627 mmol). Results from GC analysis indicated that **39–41** were present in a ratio of 10.9:1.3:1.0. The mixture was separated by gravity column chromatography (100% hexanes as eluant) to give alkene **39** in 80% yield (106.4 mg, 0.511 mmol) and alkene **41** in 7% yield (9.3 mg, 44.6 μmol) as oils.

For **39**: TLC R_f 0.67 (100% hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 120 °C, duration 2.00 min, increment rate 10 °C/min, final temperature 250 °C) t_R 4.06 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.01 (s, 9 H, $Si(CH_3)_3$), 0.89–2.12 (m, 14 H), 5.37–5.48 (m, 1 H, *H*C=C); IR (neat) 2926 (s, C—H), 2853 (s, C—H), 1736 (w, C=C), 1445 (m), 1248 (s, Si—CH_3), 1013 (w), 915 (w), 854 (s), 834 (s), 755 (w), 686 (w) cm^{-1}; EIMS *m/e* (relative intensity) 208 (8), 193 (4), 135 (11), 134 (81), 133 (7), 119 (7), 106 (5), 105 (6), 92 (15), 91 (24), 74 (7), 73 (100), 59 (12); exact mass calcd for $C_{13}H_{24}Si$ 209.1647, found (70 eV) 208.1648.

The physical and spectroscopic properties of alkene **40** are listed below.

For **41**: TLC R_f 0.67 (100% hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 120 °C, duration 2.00 min, increment rate 10 °C/min, final temperature 250 °C) t_R 4.56 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 0.89–2.12 (m, 15 H); IR (neat) 2930 (s, C—H), 2850 (s, C—H), 1710 (w, C=C), 1445 (m), 1250 (s, Si—CH_3), 1010 (w), 915 (w), 855 (s), 835 (s), 755 (w), 685 (w) cm^{-1}; EIMS *m/e* (relative intensity) 208 (5), 135 (9), 134 (64), 133 (10), 119 (6), 106 (7), 105 (5), 93 (4), 92 (9), 91 (12), 74 (8), 73 (100), 59 (12); exact mass calcd for $C_{13}H_{24}Si$ 209.1647, found (70 eV) 208.1649.

Photolysis of *trans*-6-(Oxomethyl)-5-(trimethylsilyl)bicyclo[4.4.0]-dec-1-ene (42). A solution of aldehyde **42** (142.5 mg, 0.603 mmol, 1.0 equiv) in anhydrous ethanol (16.0 mL) over anhydrous, granular potassium carbonate (159 mg) was sealed in two 10-min NMR tubes. This solution was irradiated for 21 h with UV light that was filtered through a Pyrex glass sleeve. The solution was decanted into a round-bottomed flask with diethyl ether (5 mL) and concentrated to give a mixture of alkenes **39–41** as an oil in 99% yield (124.9 mg, 0.599 mmol). Results from GC analysis indicated that **39–41** were present in a ratio of 0.1:32.0:1.0. The mixture was separated by gravity column chromatography (100% hexanes as eluant) to give alkene **40** as an oil in 96% yield (120.7 mg, 0.579 mmol).

For **40**: TLC R_f 0.67 (100% hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 120 °C, duration 2.00 min, increment rate 10 °C/min, final temperature 250 °C) t_R 4.35 min; ^1H NMR ($CDCl_3$, 80 MHz) δ 0.02 (s, 9 H, $Si(CH_3)_3$), 0.86–2.17 (m, 14 H), 5.32–5.43 (m, 1 H, *H*C=C); IR (neat) 2926 (s, C—H), 2853 (m, C—H), 1727 (w, C=C), 1446 (w), 1248 (s, Si—CH_3), 855 (s), 838 (s), 746 (w), 686 (w) cm^{-1}; EIMS *m/e* (relative intensity) 208 (11), 135 (14), 134 (89), 133 (7), 119 (9), 106 (7), 105 (6), 93 (6), 92 (15), 91 (23), 73 (100), 67 (7), 59 (10); exact mass calcd for $C_{13}H_{24}Si$ 208.1647, found (70 eV) 208.1649.

The physical and spectroscopic properties of alkenes **39** and **41** are listed above.

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