Intramolecular Anodic Olefin Coupling Reactions and the Use of Vinylsilanes

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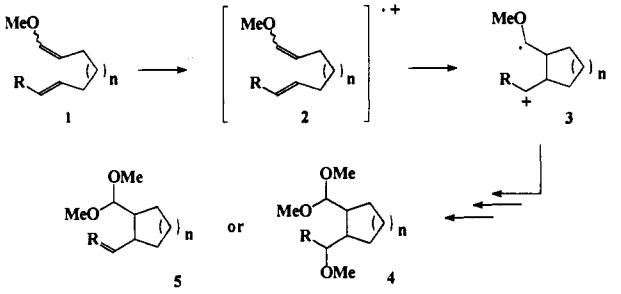
Abstract: Intramolecular anodic olefin coupling reactions involving vinylsilane groups have been studied. It was found that the previously successful predictive model for olefin coupling reactions based on an electrophilic attack of a radical cation onto an olefin did not successfully predict product formation for olefin coupling reactions involving vinylsilane terminating groups. Instead, these reactions were best described by viewing the initial addition of the radical cation to an olefin as if it occurred in a reversible "radical-like" fashion. In addition, reactions using a temporary silicon tether were shown to be compatible with the formation of quaternary carbons with control of relative stereochemistry. These reactions helped highlight the compatibility of the anodic olefin coupling reactions with extremely sensitive substrates. Finally, the results reported suggest that the mass balance of the intramolecular anodic olefin coupling reaction depends on the ease with which the initially formed cyclized product undergoes the second oxidation step.

Recently, we have reported that the intramolecular coupling of olefins at anode surfaces can provide a unique method for constructing carbon–carbon bonds.[1] These reactions can be viewed as proceeding through an initial oxidation of an enol ether to form a radical cation intermediate followed by trapping of the radical cation by a second olefin in order to form a second radical cation. Decomposition of the cyclized radical cation then leads to product. In Scheme 1, the initially formed radical cation is pictured as "attacking" the second double bond in an electrophilic fashion. This model for the reaction was based on the results of Shono and co-workers, who in 1978 reported that the anodic oxidation of enol acetates with the general structure of **6** led to the formation of six-membered ring products (Scheme 2).[2] No five-membered ring products were observed. Since a simple "radical-like" cyclization would be expected to lead to the formation of five-membered ring products,[3,4] Shono concluded that the electrochemical cyclization proceeded "through electrophilic attack of the cation center generated from the enol ester to the double bond".

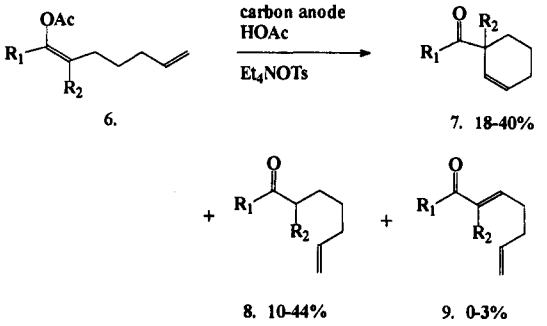
For our part, we found that viewing the cyclizations as if they were electrophilic provided a convenient model for predicting and explaining the outcome of a variety of intramolecular anodic olefin coupling reactions. For example, in analogy to the enol acetate oxidations, the cyclization of **10** led to exclusive formation of six-membered ring products (Scheme 3).[5] The formation of products **11–13** was explained by formation of a radical cation from the enol ether, electrophilic cyclization to form a six-membered ring, and then a nonselective decomposition of the resulting secondary carbocation. The lack of five-membered ring products was explained by the difficulty associated with the generation of a primary carbocation.

The formation of a product mixture that could be explained by the generation of a cation at the "terminating end" of the cyclization was a problem typical of intramolecular anodic olefin coupling reactions using simple alkyl-substituted olefins.[1a,c] Fortunately, the use of allylsilane groups circumvented this problem and led to regiochemical control of olefin formation in the product (for example, Scheme 4).[1b,c,e]

Scheme 1



Scheme 2



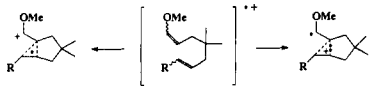
* Abstract published in *Advance ACS Abstracts*, March 15, 1994.

(1) (a) Moeller, K. D.; Marzabadi, M. R.; Chiang, M. Y.; New, D. G.; Keith, S. *J. Am. Chem. Soc.* **1990**, *112*, 6123. (b) Moeller, K. D.; Hudson, C. M. *Tetrahedron Lett.* **1991**, *32*, 2307. (c) Hudson, C. M.; Marzabadi, M. R.; Moeller, K. D.; New, D. G. *J. Am. Chem. Soc.* **1991**, *113*, 7372. (d) Moeller, K. D.; Tinao, L. V. *J. Am. Chem. Soc.* **1992**, *114*, 1033. (e) Moeller, K. D.; Hudson C. M.; Tinao-Wooldridge, L. V. *J. Org. Chem.* **1993**, *58*, 3478.

(2) Shono, T.; Nishiguchi, K.; Kashimura, S.; Okawa, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2181.

(3) (a) Walling, C.; Cooley, J. H.; Ponaras, A. A.; Racah, E. J. *J. Am. Chem. Soc.* **1966**, *88*, 5361. (b) Walling C.; Coiffari, A. *J. Am. Chem. Soc.* **1972**, *94*, 6059. For reviews see: (c) Beckwith, A. L. J. *Tetrahedron* **1981**, *31*, 3070. (d) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1.

(4) A related mechanism involving a [2 + 1] cycloaddition via a long-bond intermediate can also be proposed for these cyclization. In this mechanism the cyclic intermediate would be opened by either the attack of a nucleophile, the attack of a methoxy radical, or the loss of either a proton or trimethylsilane group.



A mechanism of this type cannot be ruled out, since for any given situation it would give rise to the same set of products that a stepwise mechanism would give rise to. However, for clarity the discussion in the text will focus solely on a stepwise picture. Similar arguments can be made for the cycloaddition based route.

(5) Unpublished results with Ryzard Pacut and Melissa Reilly.

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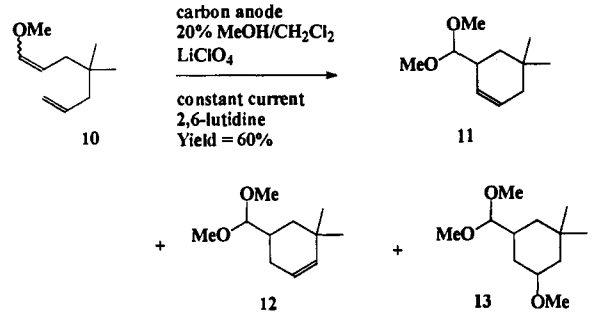
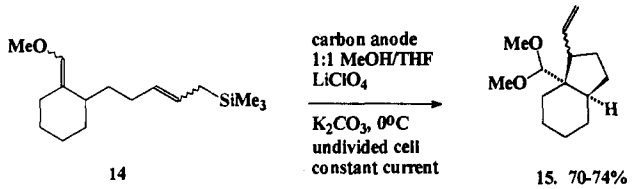
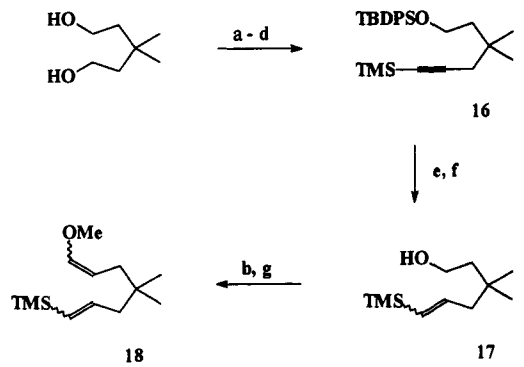
Scheme 3



Scheme 4



Scheme 5



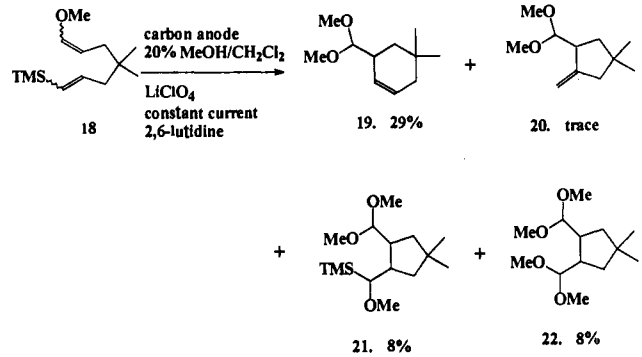
[a] Reagents: (a) TBDPSiCl, imidazole, DMF, 46%; (b) i $(COCl)_2$, DMSO, THF, ii Et_3N; (c) *t*-BuOK, Ph_3P, $CHBr_3$, toluene, −20 °C, 49% over two steps; (d) i *n*-BuLi, TMEDA, THF, −78 °C, ii TMSCl, 94%; (e) H_2, $Pd/BaSO_4$, 77%; (f) 3% HCl/CH_3OH, 0 °C, 85%; (g) $Ph_3PCHOCH_3$, THF, 0 °C, 58% over two steps.

The success of the allylsilane groups in these reactions caused us to suggest the use of vinylsilanes for controlling product formation in the coupling reactions. These reactions proved to be quite surprising. We report here that a predictive model based on an electrophilic-type cyclization does not accurately predict the outcome of anodic olefin coupling reactions involving vinylsilanes and that these reactions can best be described by a mechanism involving a reversible radical cyclization. We also report the use of a temporary silicon tether for controlling the stereochemical outcome of an electrochemical reaction.

Our initial efforts to investigate the use of vinylsilanes for controlling the regiochemistry of olefin formation in the intramolecular coupling reactions focused on the oxidation of vinylsilane substrate **18**. The synthesis of substrate **18** is outlined in Scheme 5.

The anodic oxidation of **18** using an undivided cell, a reticulated vitreous carbon (RVC) anode, 2,6-lutidine as a proton scavenger, a 0.4 M $LiClO_4$ in 20% methanol/dichloromethane electrolyte solution, and a constant current of 24.1 mA (2.2 F/mol) led to the formation of only a 29% isolated yield of the desired six-membered ring product **19** along with a 16% isolated yield of the previously unobserved five-membered ring products **21** and **22** (Scheme 6). Although not isolated, a trace amount of an additional five-membered ring product **20** was observed by NMR. The formation of five-membered ring products in this reaction was unexpected, especially in light of the earlier cyclization of substrate **10**. If the cyclizations proceeded by way of an

Scheme 6



electrophilic-type mechanism, then why would the inclusion of a trimethylsilyl group, positioned to stabilize developing carbocation character at the "terminating end" of a six-membered ring cyclization, interfere with the formation of the six-membered ring products? In this case, the trimethylsilyl directing group should have served to enhance the formation of six-membered ring products.[6] Clearly, a new way of viewing these reactions was needed.

In the 1960s, Julia pointed out that radicals stabilized by resonance with electron-withdrawing groups led to reversible cyclization reactions.[7] Could the radical cation of an enol ether initiate such a reversible cyclization reaction? If so, then a mechanism like that outlined in Scheme 7 might be operable.[4] This scheme would allow for the formation of five-membered ring cyclized radical cation intermediates like **23** along with six-membered ring radical cation intermediates like **24**. Product formation would then depend on the stability of the radical generated at the terminating end of the cyclization (**23** and **24** are essentially equivalent with respect to the resulting cation) and the ease with which such a radical would undergo the second oxidation step. For example, in the case of substrate **10** (R = H) the formation of intermediate **23a** would not be expected to lead to product formation, since a subsequent oxidation step would lead to a primary carbocation. Instead, if the cyclization were reversible, intermediate **23a** would revert to the initial radical cation and then cyclize to the six-membered ring radical cation **24a**. Subsequent oxidation of **24a** would lead to a secondary carbocation and "drain" the equilibrium toward the formation of products **11–13**. In contrast, the oxidation of substrate **18** (R = TMS) would lead to intermediate **23b**, which in turn would be oxidized to form an α-silyl cation (**26**). The α-silyl cation would be expected to either trap solvent to form product **21** or migrate a hydride to form a β-silyl carbocation that would eliminate the silane to form product **20**. Product **22** would be obtained by further oxidation of **21**.[8] The six-membered ring product formed in the oxidation of **18** would arise from a pathway that proceeded through radical cation **24b**. One might suspect that a reversible "radical-like" pathway would still favor six-membered ring formation, as observed, since intermediate **24b** would be expected to oxidize more readily than intermediate **23b**.

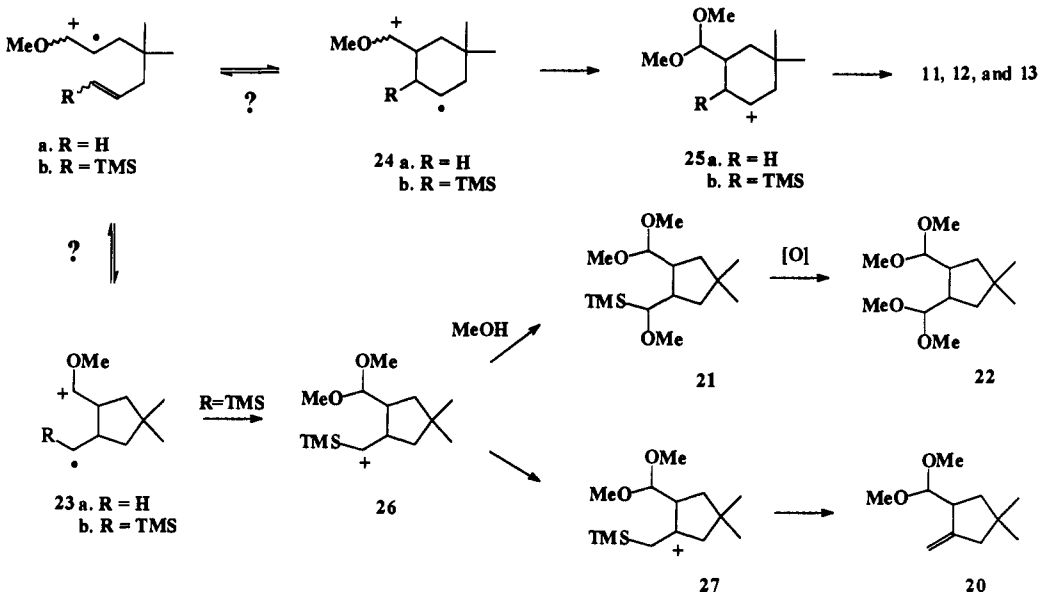
But does such an elaborate scheme make sense, and if so, how can we gain insight into how much of the product is formed through a reversible "radical-like" mechanism vs an electrophilic-type mechanism? In 1989, Miura, Oshima, and Utimoto reported that the formation of an α-silyl radical could be favored over the formation of a secondary β-silyl radical and competitive with the

(6) For a related cyclization see: Weinreb, S. M.; McIntosh, M. S. *J. Org. Chem.* **1991**, *56*, 5011.

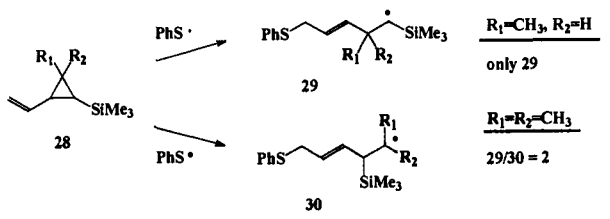
(7) (a) Julia, M. *Rec. Chem. Prog.* **1964**, *25*, 1. (b) Julia, M. *Acc. Chem. Res.* **1971**, *4*, 386.

(8) (a) Yoshida, J.; Murata, T.; Isoe, S. *Tetrahedron Lett.* **1987**, *28*, 211. (b) Yoshida, J.; Murata, T.; Isoe, S. *J. Organomet. Chem.* **1988**, *345* (3), C23. (c) Yoshida, J.; Matsunaga, S.; Isoe, S. *Tetrahedron Lett.* **1989**, *30*, 219. (d) Yoshida, J.; Maekawa, T.; Murata, T.; Matsunaga, S.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 1962. (e) Yoshida, J.; Matsunaga, S.; Murata, T.; Isoe, S. *Tetrahedron* **1991**, *47*, 615.

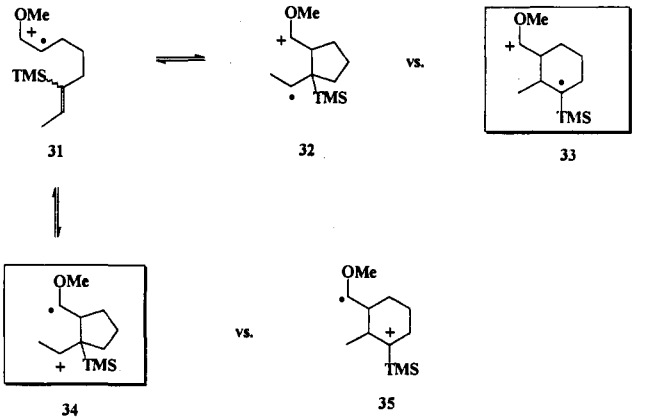
Scheme 7



Scheme 8



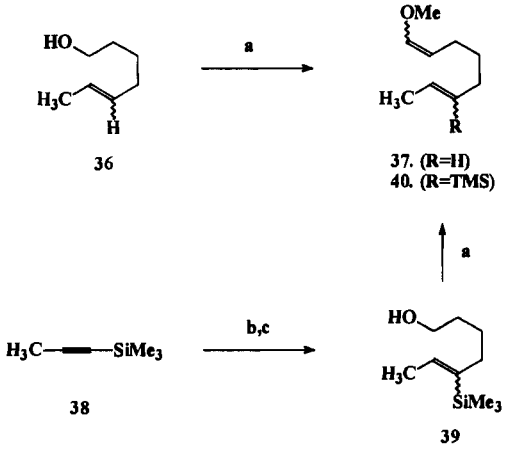
Scheme 9



formation of a tertiary β-silyl radical (Scheme 8).[9] In these studies, a phenylthio radical was used to open vinyl cyclopropane **28** in order to form either the α-silyl radical **29** or the β-silyl radical **30**. When R_1 was a methyl group and R_2 a proton, only products derived from α-silyl radical **29** were obtained. When R_1 and R_2 were both methyl groups, a 2:1 ratio of products derived from **29** to products derived from **30** was obtained. The formation of the α-silyl radical was favored even when the β-silyl radical being formed was tertiary! The preference for α-silyl radical formation in these cases is in direct contrast to what would be expected for a related cationic pathway. In such a reaction, the formation of β-silyl carbocations would be strongly favored over the formation of α-silyl carbocations.[10] At this point, we reasoned that if an analogous dichotomy existed for the anodic olefin coupling reaction, then the generation of a radical cation tethered to a properly substituted vinylsilane might provide a mechanism for probing the reversible "radical-like" vs electrophilic behavior of the olefin coupling reactions. For example, if the analogy holds, the cyclization of radical cation **31** would be expected to lead to the formation of six-membered ring products (from **33**) if the reaction followed a reversible "radical-like" pathway and five-membered ring products (from **34**) if the reaction was controlled by electrophilic factors (Scheme 9).[11]

In order to test this idea, substrates **37** and **40** were synthesized as outlined in Scheme 10. The disubstituted olefin substrate **37** was examined in order to establish the inherent tendency for five- and six-membered ring formation in the absence of the trimethylsilyl group (Scheme 11). In this experiment, compound **37** was oxidized using a reticulated vitreous carbon anode, a 0.4 M lithium perchlorate in 20% methanol/dichloromethane electrolyte solution, an undivided cell, and a constant current of 24.6 mA. The electrolysis was continued until 2 F/mol had been passed. A complex mixture of products was obtained. The crude reaction mixture was chromatographed using silica gel and 3% ether/hexane as eluant to afford the impure acetals **41–43**. The compounds were contaminated with small amounts of additional

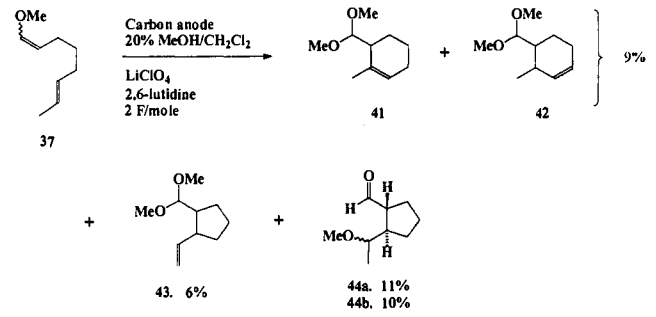
Scheme 10



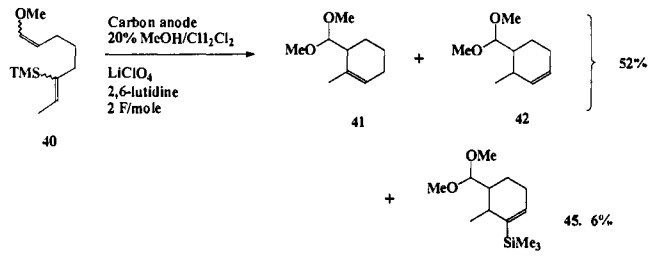
[a] Reagents: (a) i $(COCl)_2$, DMSO, THF, ii Et_3N, iii filter, iv $Ph_3PCHOCH_3$, 0 °C (R = H, 34%; R = TMS, 59%); (b) i Cp_2TiCl_2, *i*-BuMgBr, Et_2O, 0 °C, ii $I(CH_2)_4OTBDMS$; (c) 3% HCl/MeOH, 0 °C, 44% over the two steps.

(9) Miura, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1989**, *30*, 4413.
(10) For reviews of vinylsilane-terminated cyclization reactions, see: (a) Blumenkoph, T. A.; Overman, L. E. *Chem. Rev.* **1986**, *86*, 857. (b) Fleming, I.; Dunogues, J.; Smithers, R. *Org. React.* **1989**, *37*, 57.
(11) For a related cyclization, see: Mikami, K.; Kishi, N.; Nakai, T. *Tetrahedron Lett.* **1983**, *24*, 795.

Scheme 11



Scheme 12

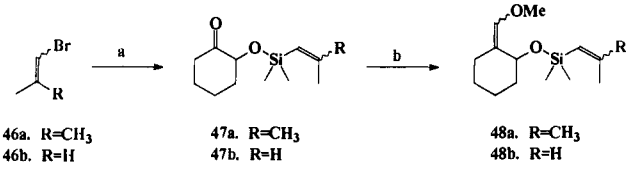


acetal products. An approximate yield (9%) for products **41** and **42** was obtained by integration of the acetal region of the ^{1}H NMR. Compounds **41** and **42** were characterized by comparison with the products of identical structure obtained from the oxidation of **40** (*vide infra*). Compound **43** was assigned as a five-membered ring product because of the presence of the terminal olefin in the ^{1}H NMR. Again an approximate yield (6%) of this product was obtained from integration of the acetal region of the ^{1}H NMR. Following isolation of the acetals, the column was flushed with ether and the remaining products were deprotected with pyridinium *p*-toluenesulfonate (PPTS) and epimerized with DBU in an attempt to decrease the number of isomers obtained. From this mixture, the diastereomeric trans ethers **44a** (11%) and **44b** (10%) were isolated. Compounds **44a** and **44b** were unequivocally assigned as five-membered ring products with the use of HMQC-TOCSY experiments.[12] Using this technique, the complete carbon and proton connectivity of **44b** was assigned.

Clearly, this reaction was a mess. However, it was readily apparent that in the absence of a trimethylsilyl group the oxidation led to a mixture of five- and six-membered ring products. In contrast, the oxidation of **40** using nearly identical conditions (in this case a constant current of 23.4 mA was used) led to the *exclusive* formation of six-membered ring products (Scheme 12). In addition to the anticipated products **41** and **42**, a small amount (*ca.* 6% by NMR integration) of a product tentatively assigned as **45** was observed in the ^{1}H NMR. This material could not be separated from **41** and **42**. *The dramatic increase in the yield of six-membered ring products and complete lack of five-membered ring products strongly suggested that the cyclization reaction proceeded through a "radical-like" mechanism.* Products **41** and **42** would arise from initial cyclization to form a tertiary α-silyl radical (**33**; Scheme 9), subsequent oxidation to a tertiary α-silyl cation, rearrangement to a β-silyl cation, and then elimination of the silyl group.

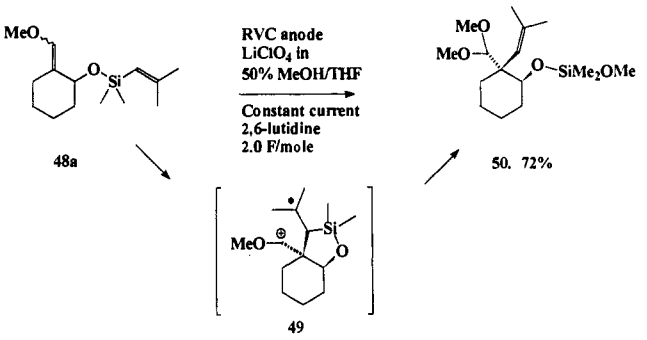
With the successful cyclization of **40**, several questions remained. Why were the mass balances of cyclization reactions involving vinylsilanes so poor? Did the vinylsilane interfere with the initial anodic oxidation step, or was there a problem with a subsequent step in the reaction? In order to investigate this question, we decided to take advantage of an empirical observation made over the last several years. When an olefin coupling reaction was predicted to form the same product from either an electrophilic-type cyclization or a kinetic "radical-like" cyclization, then the reaction would afford a good yield of product. For example, consider substrate **48a** (Scheme 13). In this case, oxidation of the enol ether followed by an electrophilic-type cyclization would be expected to lead to initial formation of a five-membered ring (and tertiary β-silyl carbocation character). Oxidation followed by a "radical-like" process would also be expected to lead to initial formation of a five-membered ring (*5-exo-trig* closure). If our earlier empirical observation held, then this anodic oxidation would afford a good yield of product, proving that the vinylsilane was stable to the anodic oxidation conditions. In addition, this reaction would represent the first use of a temporary silicon tether to control the stereochemical outcome of an electrochemical reaction.[13]

Scheme 13



[a] Reagents: (a) i *tert*-butyllithium, THF, −78 °C, ii $(CH_3)_2NSi(CH_3)_2Cl$, iii 2-hydroxycyclohexanone (reflux when R = H); (b) $Ph_3PCHOCH_3$, THF, 0 °C (R = CH_3, 35% over the two steps; R = H, 30% over the two steps).

Scheme 14



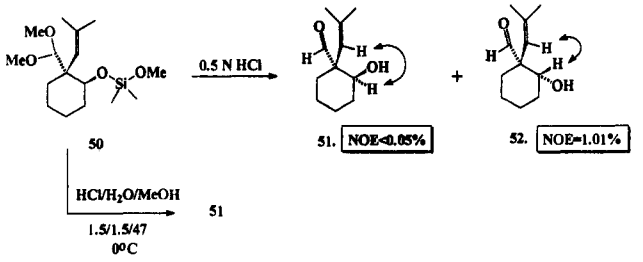
Substrate **48a** was synthesized as outlined in Scheme 13[14] and then oxidized in an undivided cell using a reticulated vitreous carbon anode, a platinum wire cathode, a 0.4 N lithium perchlorate in 50% methanol/tetrahydrofuran electrolyte solution, 2,6-lutidine as a proton scavanger, and a constant current of 24.0 mA. After 2.0 F/mol had been passed, *a 72% isolated yield of* **50** *was obtained as a single isomer* (Scheme 14). This result was exciting because it showed that vinylsilanes were compatible with the electrochemical oxidation conditions, illustrated the potential for

(12) For descriptions of the use of HMQC-TOCSY and HMBC experiments, see: (a) Martin, G. E.; Crouch, R. C. *J. Nat. Prod.* **1991**, *54*, 1. (b) Spitzer, T. D.; Crouch R. C.; Martin, G. E.; Sharaf, M. H. M.; Schiff, P. L., Jr.; Tackie, A. N.; Boye, G. L. *J. Heterocycl. Chem.* **1991**, *28*, 2065. (c) Spitzer, T. D.; Crouch, R. C.; Martin, G. E. *J. Heterocycl. Chem.* **1992**, *29*, 265. (d) Castle, L. W.; Johnston, M. D., Jr.; Camoutsis, C. L.; Castle, R. N. *J. Heterocycl. Chem.* **1992**, *29*, 1805.

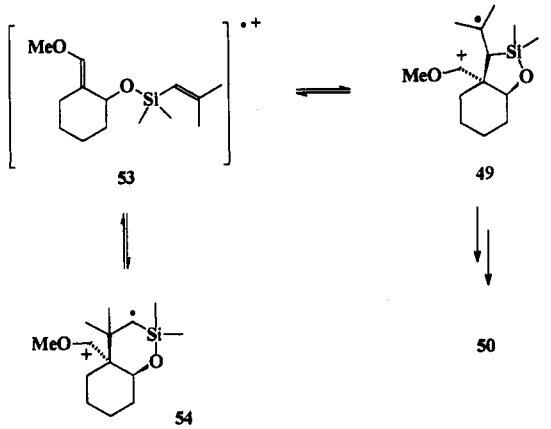
(13) For previous examples of temporary silicon tethers, please see: (a) Nishiyama, H.; Kitajima, T.; Matsumoto, M.; Itoh, K. *J. Org. Chem.* **1984**, *49*, 2298. (b) Tamao, K.; Maeda, K.; Yamaguchi, T.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 4984. (c) Koreeda, M.; Hamann, L. G. *J. Am. Chem. Soc.* **1990**, *112*, 8175. (d) Shea, K. J.; Zandi, K. S.; Staab, A. J.; Carr, R. *Tetrahedron Lett.* **1990**, *31*, 5885. (e) Shea, K. J.; Staab, A. J.; Zandi, K. S. *Tetrahedron Lett.* **1991**, *32*, 2715. (f) Stork, G. 32nd National Organic Symposium, Minneapolis, MN, June 1991. (g) Stork, G.; Suh, H. S.; Kim, G. *J. Am. Chem. Soc.* **1991**, *113*, 7054. (h) Myers, A. G.; Gin, D. Y.; Widdowson, K. L. *J. Am. Chem. Soc.* **1991**, *113*, 9661. (i) Gillard, J. W.; Fortin, W.; Grimm, E. L.; Maillard, M.; Tjepkama, M.; Bernstein, M. A.; Glaser, R. *Tetrahedron Lett.* **1991**, *32*, 1145. (j) Xi, Z.; Agback, P.; Plavec, J.; Sandstrom, A.; Chattopadhyaya, J. *Tetrahedron* **1992**, *48*, 349. (k) Stork, G.; Kim, G. *J. Am. Chem. Soc.* **1992**, *114*, 1087. (l) Stork, G.; Chan, T. Y.; Breault, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 7578. (m) Craig, D.; Reader, J. C. *Tetrahedron Lett.* **1992**, *33*, 4073. (n) Journet, M.; Malacria, M. *J. Org. Chem.* **1992**, *57*, 3085. (o) Sieburth, S. McN.; Fensterbank, L. *J. Org. Chem.* **1992**, *57*, 5279.

(14) Substrates **48a** and **48b** were made using the procedure developed by Stork: Stork, G.; Keitz, P. F. *Tetrahedron Lett.* **1989**, *30*, 6981.

Scheme 15



Scheme 16



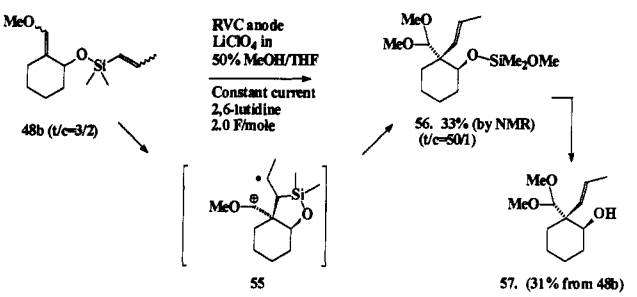
electrochemistry as a tool for synthesizing quaternary centers with control of relative stereochemistry, and demonstrated the ability of electrochemistry to initiate oxidative cyclizations with *very* acid sensitive substrates. Substrate **48a** decomposed rapidly to the corresponding α,β-unsaturated aldehyde, even on contact with triethylamine-treated silica gel.

The stereochemistry of **50** was assigned by treatment of **50** with 0.5 N HCl in water and methanol. These conditions led not only to cleavage of the acetal and the silyl ether but also to a scrambling of the alcohol stereochemistry. The stereochemistry of the alcohol could be preserved while deprotecting the acetal and the silyl ether by treatment of **50** with 1.5 mL of concentrated HCl, 1.5 mL of water, and 47 mL of methanol at 0 °C (Scheme 15). The stereochemistry of the diastereomeric alcohol aldehydes **51** and **52** was assigned using NOE difference spectroscopy. Compound **51** showed an NOE enhancement of <0.05% between the vinyl proton and the proton α to the hydroxyl group. Compound **52** showed a 1.01% NOE enhancement between the same two protons. The alcohol aldehyde obtained from **50** without scrambling of the alcohol stereochemistry proved to be compound **51**.

The formation of product **50** can be explained by the reversible "radical-like" cyclization mechanism proposed in Scheme 16. In this example, a "radical-like" cyclization would lead to either the tertiary β-silyl radical **49** or the secondary α-silyl radical **54**. Although the comparison is crude, the work of Miura, Oshima, and Utimoto cited earlier suggests that a mixture of these cyclized radicals would form. However, of the two radicals, the tertiary β-silyl radical **49** would undergo a second oxidation step much more readily than **54**. If the radical in **49** was oxidized substantially faster than the radical in **54**, then the equilibrium would be "drained" through **49** to the eventual product **50**.

A mechanism suggesting that the success of anodic olefin coupling reactions depends on the ease with which the second oxidation step occurs is tempting because it is consistent with many of the reactions studied to date. Such a suggestion would explain our empirical observation that high mass balances are obtained for cyclizations in which an electrophilic-type cyclization and/or a kinetic "radical-like" mechanism predict formation of

Scheme 17



the same product. In these cases, the "radical like" cyclization would lead to a readily oxidizable radical. In addition, many of the reactions that have led to poor mass balances involve the initial formation of more difficult to oxidize secondary radicals (see for example substrates **18** and **37**).[15] The consistency of this premise can be tested for cyclizations involving temporary silicon tethers by examining the oxidation of substrate **48b** (Scheme 17). In this example, the initial cyclization would be expected to lead to the formation of a secondary β-silyl radical and a lower mass balance of product. In practice, the oxidation of **48b** using conditions similar to those employed for the oxidation of **48a** led to the desired product **56** in poor yield (NMR yield = 33%). Compound **56** could not be isolated cleanly. Instead, the silyl ether was cleaved with tetrabutylammonium fluoride and the alcohol **57** isolated in a 31% yield over the two steps. As in the earlier case, only a single stereoisomer at the quaternary center was obtained. Compound **57** was obtained as a 50:1 mixture of trans/cis olefin isomers. For comparison, substrate **48b** was a 2:3 mixture of trans/cis olefin isomers. Variation of the reaction conditions including the use of 50% MeOH/THF as the solvent led to no change in the yield of the reaction. Clearly, the generation of a secondary radical dramatically lowered the mass balance of this reaction relative to the cyclization originating from **48a**.

In conclusion, we have found that viewing anodic olefin coupling reactions as if they involve an electrophilic type of cyclization is not effective for predicting the outcome of intramolecular reactions involving vinylsilanes. Instead, the reactions appear to proceed through a reversible "radical-like" mechanism. Once this mechanism is considered, cyclizations utilizing vinylsilanes can be designed and successfully completed even when the cyclizations are forced to generate quaternary carbons. Finally, the results reported suggest that the mass balance of the intramolecular anodic olefin coupling reaction depends on the ease with which the initially formed cyclized product undergoes the second oxidation step. Further studies aimed at exploring the mechanism and synthetic utility of these reactions in more detail are currently underway.

Experimental Section[16]

5-(*tert*-Butyldiphenylsiloxy)-3,3-dimethyl-1-pentanol. A solution of 11.1 g (84.1 mmol) of 3,3-dimethyl-1,5-pentanediol and 14.4 g (210 mmol)of imidazole in 85 mL of DMF under nitrogen was treated with 23.3 g (84.6 mmol) of *tert*-butylchlorodiphenylsilane. The reaction mixture was allowed to stir at room temperature for 64 h. The reaction was quenched with saturated sodium bicarbonate (100 mL). The layers were separated, and the aqueous layer was extracted with ether (4 × 100 mL). All the organic fractions were combined, dried over magnesium sulfate, and concentrated *in vacuo*. The crude mixture was dry-column flash-chromatographed[17] through 100 g of silica gel with a gradient elution from 100% hexane to 50% ethyl acetate/hexane to afford 14.2 g (46%) of the desired monoprotected diol. In addition 12.7 g (26%) of the diprotected diol and 0.6 g (5%) of the starting unprotected diol were obtained. The spectral data for the desired compound are as follows:

(15) See also ref 1c.
(16) For a general experimental, see: Wong, P. L.; Moeller, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 11343.
(17) Harwood, L. M. *Aldrichimica Acta* **1985**, *18*, 25.

^{1}H NMR ($CDCl_3$/300 MHz) δ 7.70–7.67 (m, 4 H), 7.44–7.36 (m, 6 H), 3.72 (t, 2 H, J = 7.1 Hz), 3.48 (dt, 2 H, J_d = 5.1 Hz, J_t = 7.5 Hz), 1.55 (t, 2 H, J = 7.1 Hz), 1.48 (t, 2 H, 7.5 Hz), 1.38 (t, 1 H, J = 5.1 Hz), 1.04 (s, 9 H), 0.86 (s, 6 H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 135.8, 134.0, 129.8, 127.8, 60.8, 59.6, 44.4, 43.9, 31.4, 27.8, 26.6, 18.8; GC/MS (PCI) m/e (relative intensity) 371 (M^+ + 1, 1.0), 313 ($M^+ - C_4H_9$, 0.6), 293 ($M^+ - C_6H_5$, 2.0), 239 (2.3), 179 (4.6), 143 (5.5), 115 ($M^+ - C_{16}H_{19}OSi$, 22), 97 (100); HRMS (EI) m/e calcd for $C_{19}H_{25}O_2Si$ ($M^+ - C_4H_9$) 313.1623, found 313.1608.

1,1-Dibromo-6-(*tert*-butyldiphenylsiloxy)-4,4-dimethyl-1-hexene. A stirred solution of 14.2 g (38.4 mmol) of 5-(*tert*-butyldiphenylsiloxy)-3,3-dimethyl-1-pentanol and 3.74 g (47.9 mmol) of DMSO in 115 mL of THF at –60 °C under nitrogen was treated with 5.53 g (43.6 mmol) of oxalyl chloride. The resulting mixture was stirred for 20 min at –60 °C, quenched with 12.1 g (120 mmol) of triethylamine, and warmed to room temperature. The reaction mixture was filtered to remove the insoluble salts and concentrated *in vacuo*. The crude mixture was filtered through 20 g of silica gel with 100% ether, dried over potassium carbonate, and concentrated *in vacuo*. In a separate flask 16.9 g (151 mmol) of potassium *tert*-butoxide and 39.4 g (150 mmol) of triphenylphosphine in 550 mL of toluene at –20 °C under nitrogen was treated with 37.6 g (149 mmol) of bromoform. After the reaction mixture was stirred for 15 min at –20 °C, a solution of the crude aldehyde formed above in 80 mL of toluene was added dropwise over 15 min. The ice bath was removed and the reaction mixture stirred for 45 min while being warmed to room temperature. The crude reaction mixture was filtered through Celite and concentrated *in vacuo*. The material was chromatographed through 100 g of silica gel with hexane as the eluant to afford 9.91 g (49%) of the desired product. The spectral data are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 7.69–7.66 (m, 4 H), 7.44–7.38 (m, 6 H), 6.41–6.36 (app t, 1 H, vinyl proton at C_2), 3.71 (t, 2 H, J = 7.1 Hz), 1.99 (d, 2 H, J = 7.4 Hz), 1.53 (t, 2 H, J = 7.1 Hz), 1.04 (s, 9 H), 0.88 (s, 6 H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 136.4, 135.8, 133.9, 129.8, 127.8, 89.4, 60.7, 45.3, 43.6, 33.2, 27.2, 26.6, 18.9; IR (neat/NaCl) 3078, 3056, 2961, 2924, 2859, 1615, 1593, 1468, 1432, 1388, 1359, 1117, 817 cm^{-1}; GC/MS (PCI) m/e (relative intensity) 525 (M^+ + 1, 0.13), 467 ($M^+ - C_4H_9$, 1.1), 445 (M^+ – Br, 1.4), 447 ($M^+ - C_6H_5$, 2.6), 269 ($M^+ - C_{16}H_{19}OSi$, 1.6), 187 (12), 129 (4), 108 (23), 97 (5.1), 81 (2.6), 79 (2.4); HRMS (EI) m/e calcd for $C_{20}H_{23}OSi^{79}Br^{81}Br$ ($M^+ - C_4H_9$) 466.9864, found 466.9855.

6-(*tert*-Butyldiphenylsiloxy)-4,4-dimethyl-1-(trimethylsilyl)-1-hexyne (16). To a stirred solution of 9.70 g (18.5 mmol) of 1,1-dibromo-6-(*tert*-butyldiphenylsiloxy)-4,4-dimethyl-1-hexene and 8.5 mL (53.1 mmol) of TMEDA in 55 mL of THF at –78 °C was added 18.5 mL (46.2 mmol) of a 2.5 M *n*-butyllithium in hexane solution. The reaction mixture was stirred an additional 1.5 h at –78 °C. Chlorotrimethylsilane, 3.11 g (28.7 mmol), was added and the reaction mixture stirred for 2 h at –78 °C followed by 3 h at room temperature. The reaction was quenched with 100 mL of saturated sodium bisulfate and 100 mL of ether. The layers were separated and the aqueous layer extracted twice with ether (100 mL). All organic fractions were combined, dried over potassium carbonate, and concentrated *in vacuo*. The crude material was chromatographed through 125 g of silica gel that was packed with 100% hexane containing 1% triethylamine. The column was eluted using 100% hexane to afford 7.60 g (94%) of the desired product. The spectral data are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 7.69–7.66 (m, 4 H), 7.42–7.36 (m, 6H), 3.71 (t, 2 H, J = 7.0 Hz), 2.10 (s, 2 H), 1.63 (t, 2 H, J = 7.0 Hz), 1.03 (s, 9 H), 0.92 (s, 6 H), 0.13 (s, 9 H); ^{13}C NMR ($CDCl_3$/75 MHz) 135.8, 134.1, 129.7, 127.8, 105.7, 86.3, 60.9, 43.1, 33.4, 32.7, 26.8, 26.6, 18.9, –0.11; IR (neat/NaCl) 3071, 3052, 3015, 3000, 2943, 2928, 2885, 2175, 1590, 1473, 1428, 1250, 1114, 1104, 1051, 1006, 855 cm^{-1}; GC/MS (PCI) m/e (relative intensity) 437 (M^+ + 1, 11), 436 (M^+, 0.6), 421 ($M^+ - CH_3$, 20), 379 ($M^+ - C_4H_9$, 19), 359 ($M^+ - C_6H_5$, 29), 209 ($M^+ - C_{16}H_{19}Si$, 9.0), 193 ($M^+ - C_{16}H_{19}SiO$, 1.9), 181 (33), 179 (14), 135 (10), 109 (100), 73 (66); HRMS (EI) m/e calcd for $C_{23}H_{31}OSi_2$ ($M^+ - C_4H_9$) 379.1915, found 379.1919.

(*E* and *Z*)-6-(*tert*-Butyldiphenylsiloxy)-4,4-dimethyl-1-(trimethylsilyl)-1-hexene. A solution of 7.41 g (17.0 mmol) of 6-(*tert*-butyldiphenylsiloxy)-4,4-dimethyl-1-(trimethylsilyl)-1-hexyne and 1.08 g of 5% palladium on barium sulfate in 48 mL of pyridine was allowed to stir for 20 h under 1 atm of hydrogen at room temperature. TLC showed unreacted starting material, so an additional 0.72 g of 5% palladium on barium sulfate was added and the reaction mixture allowed to stir an additional 7 h under 1 atm of hydrogen. The reaction mixture was diluted with ether, filtered through silica gel, and concentrated *in vacuo*. The crude material was chromatographed through 125 g of silica gel that was packed with 100% hexane containing 1% triethylamine and eluted with 100% hexane to remove the pyridine. All of the fractions containing product were combined, concentrated *in vacuo*, and subjected to a second chromatography through 125 g of silica gel that was packed with 100% hexane containing 1% triethylamine. The column was eluted with 100% hexane to afford 5.72 g (77%) of the desired vinylsilane as a clear colorless oil and 1.15 g (16%) of recovered starting material. The spectral data for the mixture of olefin isomers are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 7.77–7.74 (m, 4 H), 7.48–7.44 (m, 6 H), 6.35 (dt, 0.8 H, J_d = 14.2 Hz, J_t = 7.2 Hz, C_2 vinyl proton in the cis isomer), 6.07 (dt, 0.2 H, J_d = 18.3 Hz, J_t = 7.0 Hz, C_2 vinyl proton in the trans isomer), 5.66 (dd, 0.2 H, J_1 = 18.6 Hz, J_2 = 1.4 Hz, C_1 vinyl proton in the trans isomer), 5.59 (dd, 0.8 H, J_1 = 14.2 Hz, J_2 = 1.4 Hz, C_1 vinyl proton in the cis isomer), 3.80 (t, 2 H, J = 7.5 Hz), 2.08–2.03 (m, 2 H), 1.66–1.56 (m, 2 H), 1.12 (s, 9 H), 0.91, 0.89 (two s, 6 H), 0.15, 0.11 (two s, 9 H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 145.4, 143.8, 135.6, 134.0, 133.1, 130.6, 129.5, 127.6, 60.9, 50.0, 45.7, 44.2, 44.0, 32.7, 32.5, 27.3, 26.9, 19.1, 0.4, –1.1; IR (neat/NaCl) 3071, 3051, 2956, 2929, 2894, 2858, 1604, 1591, 1473, 1463, 1428, 1365, 1248, 1113, 1105, 1092, 1006, 998, 860, 836, 735, 709, 687, 613 cm^{-1}; GC/MS (PCI) m/e (relative intensity) for the trans isomer 439 (M^+ + 1, 0.6), 438 (M^+, 0.2), 423 ($M^+ - CH_3$, 1.3), 3.61 ($M^+ - C_6H_5$, 1.1), 313 (4.3), 251 (15), 211 ($M^+ - C_{16}H_{19}Si$, 9.1), 195 ($M^+ - C_{16}H_{19}SiO$, 4.5), 175 (11), 147 (15), 135 (12), 109 (12), 73 (100); GC/MS (PCI) m/e (relative intensity) for the cis isomer 439 (M^+ + 1, 0.9), 438 (M^+, 0.2), 423 ($M^+ - CH_3$, 1.5), 3.61 ($M^+ - C_6H_5$, 1.4), 313 (2.8), 251 (15), 211 ($M^+ - C_{16}H_{19}Si$, 12), 195 ($M^+ - C_{16}H_{19}SiO$, 5.0), 175 (11), 147 (15), 135 (13), 109 (13), 73 (100); HRMS (EI) m/e calcd for $C_{23}H_{33}OSi_2$ ($M^+ - C_4H_9$) 381.2069, found 381.2060.

(*E* and *Z*)-3,3-Dimethyl-6-(trimethylsilyl)-5-hexen-1-ol (17). A solution of 2.17 g (4.96 mmol) of (*E* and *Z*)-6-(*tert*-butyldiphenylsiloxy)-4,4-dimethyl-1-(trimethylsilyl)-1-hexene in 25 mL of 3% HCl/methanol was allowed to stir for 6 h at 0 °C. The reaction mixture was diluted with ether (25 mL) and washed with saturated sodium bicarbonate (2 × 25 mL). The organic fraction was dried over potassium carbonate, concentrated *in vacuo*, and dry-column flash-chromatographed through 30 g of silica. A gradient of 100% hexane to 30% ethyl acetate/hexane was used to afford 0.84 g (85%) of the desired product. The spectral data are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 6.38–6.28 (m, 0.83 H, C_5 vinyl proton in the cis isomer), 5.99 (dt, 0.17 H, J_d = 18.4 Hz, J_t = 7.1 Hz, C_5 vinyl proton in the trans isomer), 5.61 (d, 0.17 H, J = 18.3 Hz), 5.54 (d, 0.83 H, J = 14.2 Hz), 3.68 (t, 2 H, J = 7.7 Hz), 2.04 (dd, 1.66 H, J_1 = 7.3 Hz, J_2 = 1.5 Hz), 2.00 (d, 0.34 H, J = 7.1 Hz), 1.53 (t, 2 H, J = 7.7 Hz), 1.46 (s, 1 H), 0.90 (s, 5 H, gem methyl protons in the cis isomer), 0.87 (s, 1 H, gem methyl protons in the trans isomer), 0.08 (s, 7.5 H, trimethylsilyl protons in the cis isomer), 0.02 (s, 1.5 H, trimethylsilyl protons in the trans isomer); ^{13}C NMR ($CDCl_3$/75 MHz) δ 145.0, 143.4, 133.4, 130.9, 59.7, 50.0, 45.6, 44.6, 44.0, 32.7, 32.5, 27.2, 0.3, –1.2; IR (neat/NaCl) 3319, 2954, 2896, 1607, 1471, 1387, 1247, 1031, 860 cm^{-1}; GC/MS (PCI) m/e (relative intensity) first peak 201 (M^+ + 1, 0.1), 185 ($M^+ - CH_3$, 3.9), 169 ($M^+ - CH_3O$, 1.0), 155 ($M^+ - C_2H_5O$, 1.6), 141 (1.2), 127 ($M^+ - C_3H_9OSi$, 0.7), 109 (21), 101 ($M^+ - C_5H_{11}Si$, 6.0), 95 (8.1), 83 (19), 73 (64), 69 (100); GC/MS (PCI) m/e (relative intensity) second peak 201 (M^+ + 1, 0.1), 185 ($M^+ - CH_3$, 9.7), 169 ($M^+ - CH_3O$, 1.0), 167 (12), 155 ($M^+ - C_2H_5O$, 1.8), 141 (2.0), 127 ($M^+ - C_3H_9OSi$, 1.0), 109 (16.3), 101 ($M^+ - C_5H_{11}Si$, 6.7), 95 (9.8), 83 (23), 73 (60), 69 (100); HRMS (EI) m/e calcd for $C_{11}H_{24}OSi$ 200.1596, found 200.1570.

(*E* and *Z*)-4,4-Dimethyl-1-methoxy-7-(trimethylsilyl)-1,6-heptadiene (18). To a stirred solution of 3.7 g (11 mmol) of (methoxymethyl)-triphenylphosphonium chloride in 20 mL of THF at 0 °C was added dropwise 7.7 mL (11 mmol) of a 1.5 M *tert*-butyllithium in hexane solution. The resulting dark-red solution was allowed to warm to room temperature and stirred for 1 h. In a separate reaction flask a stirred solution of 0.54 g (2.7 mmol) of (*E* and *Z*)-3,3-dimethyl-6-(trimethylsilyl)-5-hexen-1-ol (17) and 0.25 g (3.2 mmol) of DMSO in 9 mL of THF at –78 °C was treated with 0.37 g (2.9 mmol) of oxalyl chloride. The resulting mixture was stirred for 15 min, and then the reaction was quenched with 0.84 g (8.3 mmol) of triethylamine. The ice bath was removed and the reaction mixture stirred for 15 min at room temperature. The reaction mixture was diluted with 9 mL of THF, filtered to remove the insoluble salts, and added dropwise to a 0 °C solution of the ylide generated above. The resulting mixture was allowed to warm to room temperature. After 16 h the mixture was diluted with ether (25 mL) and washed with saturated ammonium chloride (25 mL) and brine (25 mL). The organic fraction was dried over potassium carbonate, concentrated *in vacuo*, diluted with hexane to precipitate the triphenylphosphine oxide, and concentrated *in vacuo*. The product was chromatographed through 50 g of silica gel that

was packed with 100% hexane containing 1% triethylamine. The column was eluted with 100% hexane to afford 0.35 g (58%) of the desired enol ether **18**. The spectral data for the mixture of olefin isomers are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 6.41–5.90 (m, 2 H), 5.64–5.48 (m, 1 H), 4.70 (dt, 0.45 H, J_d = 12.5 Hz, J_t = 7.9 Hz), 4.35 (dd, 0.55 H, J_1 = 7.8 Hz, J_2 = 14.2 Hz), 3.54, 3.50 (two s, 3H), 2.05–1.92 (m, 3.1 H), 1.80 (d, 0.6 H, J = 7.9 Hz), 1.76 (d, 0.3 H, J = 8.7 Hz), 0.85, 0.83, 0.82, 0.814, 0.808, 0.79 (six s, 6 H), 0.10, 0.09, 0.08, 0.02, –0.05, (five s, 9 H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 148.4, 147.3, 147.1, 146.0, 145.6, 144.4, 143.9, 133.0, 132.7, 130.5, 130.2, 103.2, 99.2, 99.0, 59.4, 55.9, 49.2, 44.8, 40.5, 40.1, 36.3, 35.9, 33.9, 33.8, 33.7, 26.6, 0.4, –1.1; IR (neat/NaCl) 3040, 2947, 1666, 1653, 1603, 1468, 1391, 1383, 1365, 1245, 1210, 1116, 1111, 841, 834 cm^{-1}; GC/MS (PCI) *m/e* (relative intensity) first peak 227 (M^+ + 1, 0.6), 226 (M^+, 0.6), 225 (M^+ – 1, 1.1), 211 (M^+ – CH_3, 30), 155 (M^+ – C_4H_7O, 22), 123 (73), 113 (M^+ – $C_6H_{13}Si$, 9.4), 95 (14), 73 (100); GC/MS (PCI) *m/e* (relative intensity) second peak 227 (M^+ + 1, 1.8), 226 (M^+, 2.2), 225 (M^+ – 1, 3.2), 211 (M^+ – CH_3, 84), 155 (M^+ – C_4H_7O, 1.6), 123 (100), 113 (M^+ – $C_6H_{13}Si$, 12), 95 (14), 73 (89); HRMS (EI) *m/e* calcd for $C_{13}H_{26}OSi$ 226.1752, found 226.1756.

Electrolysis of Compound 18. Synthesis of 5,5-Dimethyl-2-cyclohexene-1-carboxaldehyde Dimethyl Acetal (19), 4,4-Dimethyl-2-(1-methoxy-1-(trimethylsilyl)methyl)cyclopentane-1-carboxaldehyde Dimethyl Acetal (21), and 4,4-Dimethyl-1,2-bis(dimethoxymethyl)cyclopentane (22). A mixture of 0.242 g (1.07 mmol) of (*E* and *Z*)-4,4-dimethyl-1-methoxy-7-(trimethylsilyl)-1,6-heptadiene, 0.34 g (3.2 mmol) of 2,6-lutidene, and 4.0 g of lithium perchlorate in 95 mL of a 1:4 methanol/dichloromethane solution was placed in a three-necked round-bottom flask equipped with a reticulated vitreous carbon anode (suspended from a carbon rod), a carbon-rod cathode, and a nitrogen inlet. The reaction mixture was degassed via sonication (5 min) and electrolyzed at a constant current of 24.1 mA until 225 C (2.2 F/mol) of charge had been passed. When the reaction was complete, the reaction mixture was transferred to a separatory funnel and washed with water (2 × 25 mL). The aqueous fractions were combined and extracted with dichloromethane (2 × 25 mL). The organic fractions were combined, dried over potassium carbonate, concentrated *in vacuo* and chromatographed through 75 g of silica gel that was slurry packed with a hexane solution containing 1% triethylamine. The column was eluted with 100% hexane to afford 0.026 g (8%) of **21**, 0.020 g (8%) of **22**, and two impure fractions, 0.044 g each, containing some **19**. These fractions were determined to contain a total of 0.054 g (29%) of **19** based on the acetal protons in the ^{1}H NMR. The spectral data for the impure compound **19** are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 5.68 (A of AB, 1 H, J_{ab} = 10 Hz with fine coupling), 5.61 (B of AB, 1 H, J_{ab} = 10 Hz), 4.03 (d, 1 H, J = 7.1 Hz), 3.36, 3.33 (two s, 6 H), 2.42 (br, 1 H), 1.83 (A of AB, 1 H, J_{ab} = 17.9 Hz), 1.69 (B of AB, 1 H, J_{ab} = 17.9 Hz), 1.44–1.38 (m, 1 H), 1.21–1.01 (m, 1 H plus impurities), 0.85, 0.93 (two s, 6H); ^{13}C NMR ($CDCl_3$/75 MHz) 127.9, 125.1, 107.8, 53.9, 53.5, 39.1, 37.6, 36.8, 32.0, 29.0, 25.2; GC/MS (PCI) *m/e* (relative intensity) 185 (M^+ + 1, 6.5), 184 (M^+, 1.4), 183 (M^+ – 1, 5.2), 153 (M^+ – CH_3O, 100), 139 (12), 121 (46), 105 (18), 75 (92). The spectral data for **21** are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 4.41 (d, 1 H, J = 4.6 Hz), 3.91, 3.37, 3.34 (three s, 9 H), 2.81 (d, 1 H, J = 8.2 Hz), 2.34–2.10 (m, 2 H), 1.57–1.46 (m, 4 H), 0.98, 0.96 (two s, 6 H), 0.04 (s, 9 H); ^{13}C NMR ($CDCl_3$/75 MHz) 109.1, 81.9, 60.4, 55.6, 55.2, 47.4, 45.4, 43.1, 40.3, 38.0, 30.6, 29.6, –1.9; GC/MS (PCI) *m/e* (relative intensity) 288 (M^+, 0.11), 287 (M^+ – 1, 0.31), 257 (M^+ – CH_3O, 2.1), 242 (M^+ – C_2H_6O, 3.9), 241 (12), 226 (M^+ – $C_2H_6O_2$, 9.0), 225 (28), 184 (M^+ – $C_4H_{12}OSi$, 3.2), 183 (13), 153 (184 – CH_3O, 58), 121 (92), 89 (22), 75 (100); HRMS (EI) *m/e* calcd for $C_{13}H_{25}O_2Si$ (M^+ – C_2H_7O) 241.1623, found 241.1614. The spectral data for compound **22** matched that previously reported.[1d]

(*E* and *Z*)-1-Methoxy-1,6-octadiene (37). To a stirred solution of 20.6 g (60 mmol) of (methoxymethyl)triphenylphosphonium chloride in 60 mL of THF at 0 °C was added dropwise 40 mL (60 mmol) of a 1.5 M *tert*-butyllithium in hexane solution. The resulting dark-red solution was allowed to warm to room temperature and stirred for 1 h. In a separate flask a stirred solution of 1.4 g (18 mmol) of DMSO and 1.7 g (15 mmol) of 5-hepten-1-ol in 40 mL of THF at –60 °C was treated with 2.2 g (17.2 mmol) of oxalyl chloride. The reaction temperature was decreased to –78 °C, the reaction mixture stirred for 15 min, and then the reaction quenched with 4.7 g (46 mmol) of triethylamine. The ice bath was removed and the reaction allowed to stir for 15 min at room temperature. The crude mixture was diluted with 30 mL of THF and filtered to remove the insoluble salts. The salts were washed with an additional 30 mL of THF. The filtrate was then added dropwise to a 0 °C solution of the ylide generated above. The resulting reaction mixture was allowed to warm to room temperature. After 16 h the mixture was diluted with 100 mL of ether and washed with saturated ammonium chloride (2 × 150 mL). The aqueous fractions were combined and extracted with ether (2 × 150 mL). The organic fractions were combined, dried over potassium carbonate, and concentrated *in vacuo*. The crude mixture was diluted with hexane to precipitate the triphenylphosphine oxide, filtered, concentrated *in vacuo*, and chromatographed through 100 g of silica gel slurry packed with a 1% triethylamine in hexane solution. The column was eluted with hexane to afford 0.71 g (34%) of the desired enol ether **37**. The spectral data for the mixture of olefin isomers are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 6.26 (d, 0.57 H, J = 12.6 Hz), 5.86–5.83 (m, 0.43 H), 5.45–5.32 (m, 2 H), 4.70 (dt, 0.57 H, J_d = 12.6 Hz, J_t = 7.3 Hz), 4.35–4.28 (m, 0.43 H), 3.55, 3.47 (two s, 3 H), 2.09–1.97 (m, 2 H), 1.91 (dd, 2 H, J_1 = 14.6 Hz, J_2 = 7.2 Hz), 1.61 (d, 0.79 H, J = 4.0 Hz), 1.58 (d, 2.21 H, J = 5.2 Hz), 1.42–1.33 (m, 2 H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 147.1, 146.1, 131.4, 131.2, 130.6, 130.4, 124.9, 123.9, 123.8, 106.7, 102.9, 59.4, 55.8, 32.2, 31.9, 30.6, 29.7, 27.2, 27.1, 26.5, 26.1, 23.5, 23.4, 17.9, 12.8; IR (neat/NaCl) 3013, 2930, 2855, 1664, 1656, 1456, 1262, 1210, 1111 cm^{-1}; GC/MS (PCI) *m/e* (relative intensity) 141 (M^+ + 1, 3.1), 140 (M^+, 0.36), 139 (M^+ – 1, 1.16), 109 (M^+ – CH_3O, 45), 81 (11), 71 (100).

Electrolysis of Compound 37. A solution of 4.1 g of lithium perchlorate in 95 mL of 20% methanol/dichloromethane containing 0.143 g (1.0 mmol) of compound **37** and 0.29 g (2.7 mmol) of 2,6-lutidine was placed in a three-necked round-bottom flask equipped with a reticulated vitreous carbon anode (suspended from a carbon rod), a carbon-rod anode, and a nitrogen inlet. The reaction mixture was degassed via sonication (5 min) and electrolyzed at a constant current of 24.6 mA until 197 C (2 F/mol) of charge had been passed. When the reaction was complete, the reaction mixture was washed with water (2 × 50 mL). The aqueous fractions were combined and extracted with dichloromethane (2 × 50 mL). All organic fractions were combined, dried over potassium carbonate, and concentrated *in vacuo*. The crude reaction mixture was chromatographed through 30 g of silica gel that was slurry packed with 100% hexane containing 1% triethylamine. Gradient elution from 100% hexane to 3% ether/hexane afforded 0.025 g of an impure mixture of 2-methyl-2-cyclohexene-1-carboxaldehyde dimethyl acetal (**41**) and 2-methyl-3-cyclohexene-1-carboxaldehyde dimethyl acetal (**42**). These products were identified by comparison with the cyclohexene products formed in the electrolysis of compound **40** (*vide infra*). This fraction was estimated to contain 0.016 g (9%) of compounds **41** and **42** based on the acetal protons in the ^{1}H NMR. A second fraction was isolated that contained 0.023 g of an impure product. This product was tentatively assigned as 2-ethenylcyclopentane-1-carboxaldehyde dimethyl acetal (**43**) on the basis of the presence of the terminal olefin protons in the ^{1}H NMR. An approximate yield for **43** was calculated to be 0.011 g (6%) based on integration of the acetal region in the ^{1}H NMR. After these products were isolated, the column was flushed with 150 mL of ether and all the eluant combined, washed with 0.5 N HCL (10 mL) to remove the 2,6-lutidene, and concentrated *in vacuo*. This fraction was diluted with 10 mL of acetone and treated with 0.1 g (0.4 mmol) of PPTS for 16 h at room temperature. The reaction was diluted with 10 mL of water, the acetone was removed *in vacuo*, the aqueous fraction was extracted with ether (3 × 20 mL), and the organic layers were dried over magnesium sulfate and concentrated *in vacuo*. The crude aldehyde mixture was diluted with 10 mL of dichloromethane and treated with 0.05 mL of DBU at room temperature for 64 h. The reaction mixture was concentrated and placed directly onto a column containing 30 g of silica gel packed with 1% ether/hexane. The product was eluted with 1% ether/hexane to afford 0.018 g (11%) and 0.016 g (10%) of two isomers of 2-(1-methoxyethyl)cyclopentane-1-carboxaldehyde (**44a** and **44b**). The spectral data for the first isomer **44a** are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 9.62 (d, 1 H, J = 2.8 Hz), 3.32 (s, 3 H), 3.30–3.26 (m, 1 H), 2.64 (dq, 1 H, J_d = 2.8 Hz, J_q = 7.8 Hz), 2.32 (dq, 1 H, J_d = 5.3 Hz, J_q = 8.0 Hz), 1.90–1.50 (m, 6 H), 1.13 (d, 3 H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$/75 MHz) δ 204.1, 78.1, 56.5, 53.8, 46.1, 27.8, 27.3, 25.4, 16.7; IR (neat/NaCl) 2934, 2873, 1718, 1457 cm^{-1}; GC/MS (PCl) *m/e* (relative intensity) 157 (M^+ + 1, 3.9), 156 (M^+, 18), 155 (M^+ – 1, 100), 141 (M^+ – CH_3, 4.8), 127 (M^+ – CHO, 45), 125 (M^+ – CH_3O, 26), 113 (49), 97 (M^+ – C_3H_7O, 14), 95 (94), 75 (81); HRMS (EI) *m/e* calcd for $C_8H_{13}O_2$ (M^+ – CH_3) 141.0915, found 141.0926. The spectral data for the second isomer **44b** are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 9.59 (d, 1 H, J = 3.2 Hz), 3.29 (s, 3 H), 3.09 (dq, 1 H, J_d = 3.6 Hz, J_q = 6.0 Hz), 2.58 (dq, 1 H, J_d = 3.0 Hz, J_q = 8.0 Hz), 2.20 (p, 1 H, J = 8.4 Hz), 1.93–1.19 (m, 6 H), 1.15 (d, 3 H, J = 6.0 Hz); ^{13}C NMR

($CDCl_3$/75 MHz) δ 204.0, 80.7, 56.3, 55.9, 48.5, 29.4, 26.8, 25.1, 17.4; IR (neat/NaCl) 2957, 2872, 1722, 1457 cm^{-1}; GC/MS (PCI) *m/e* (relative intensity) 157 (M^+ + 1, 2.3), 156 (M^+, 7.8), 155 (M^+ – 1, 73), 141 (M^+ – CH_3, 78), 123 (53), 95 (100); HRMS (EI) *m/e* calcd for $C_8H_{13}O_2$ (M^+ – CH_3) 141.0915, found 141.0961.

4-(*tert*-Butyldimethylsiloxy)butyl *p*-Toluenesulfonate. To a solution of 14.8 g (73 mmol) of 4-(*tert*-butyldimethylsiloxy)-1-butanol and 6.4 g (80 mmol) of pyridine in 100 mL of dichloromethane was added 15.3 g (80 mmol) of *p*-toluenesulfonyl chloride. The reaction mixture was allowed to stir for 16 h at room temperature and then washed with saturated sodium bicarbonate (2 × 100 mL). The aqueous fractions were combined and extracted with dichloromethane (2 × 100 mL). All organic fractions were combined, dried over magnesium sulfate, concentrated *in vacuo*, and chromatographed through 150 g of silica gel with a gradient elution from 5% ether/hexane to 10% ether/hexane as the eluant to afford 17.9 g (69%) of the desired product. The spectral data are as follows: ^1H NMR ($CDCl_3$/300 MHz) δ 7.75 (d, 2 H, *J* = 8.2 Hz), 7.30 (d, 2 H, *J* = 7.9 Hz), 4.01 (t, 2 H, *J* = 6.6 Hz), 3.51 (t, 2 H, *J* = 6.0 Hz), 2.40 (s, 3 H), 1.74–1.64 (m, 2 H), 1.53–1.44 (m, 2 H), 0.81 (s, 9 H), –0.04 (s, 6 H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 144.8, 133.3, 130.0, 128.0, 70.6, 62.0, 28.3, 25.6, 25.3, 21.4, 18.0, –5.8; IR (neat/NaCl) 2952, 2886, 2856, 1599, 1471, 1368, 1170, 1096, 834.

4-(*tert*-Butyldimethylsiloxy)-1-iodobutane. A solution of 1.8 g (5 mmol) of 4-(*tert*-butyldimethylsiloxy)butyl *p*-toluenesulfonate and 2.0 g (13 mmol) of sodium iodide in 25 mL of freshly distilled acetone was heated to reflux for 16 h. After cooling and filtration of the sodium tosylate, the acetone was removed *in vacuo* and the oily residue taken up in 100 mL of ether. The ether solution was washed with saturated sodium thiosulfate (50 mL), dried over magnesium sulfate, concentrated *in vacuo*, and chromatographed through 25 g of silica gel with 100% hexane as the eluant to afford 1.3 g (81%) of the desired product. The spectral data are as follows: ^1H NMR ($CDCl_3$/300 MHz) δ 3.60 (t, 2 H, *J* = 6.1 Hz), 3.18 (t, 2 H, *J* = 7.0 Hz), 1.91–1.82 (m, 2 H), 1.62–1.53 (m, 2 H), 0.85 (s, 9 H), 0.00 (s, 6 H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 61.8, 33.3, 30.0, 25.7, 18.0, 6.8, –5.6; GC/MS (PCI) *m/e* (relative intensity) 315 (M^+ + 1, 1.1), 314 (M^+, 0.96), 299 (M^+ – CH_3, 18), 257 (M^+ – C_4H_9, 26), 187 (M^+ – I, 97), 183 (100); HRMS (EI) *m/e* calcd for $C_9H_{20}OSiI$ (M^+ – CH_3) 299.0330, found 299.0351.

(*E* and *Z*)-5-(Trimethylsilyl)-5-hepten-1-ol (39). A solution of 0.13 g (0.52 mmol) of titanocene dichloride in 10 mL of ether at 0 °C was treated with 5.6 mL (11 mmol) of a 2.0 M solution of isobutylmagnesium bromide in ether. The resulting solution was stirred for 30 min at 0 °C, treated with 1.1 g (10 mmol) of 1-(trimethylsilyl)-1-propyne, and allowed to warm to room temperature. After 16 h the ether was removed under a stream of nitrogen and the reaction mixture diluted with 15 mL of THF. In a separate flask, a solution of 1.29 g (4.1 mmol) of 4-(*tert*-butyldimethylsiloxy)-1-iodobutane and 0.11 g (0.58 mmol) of cuprous iodide in 6 mL of THF at –30 °C was treated dropwise with the Grignard reagent formed above. The reaction mixture was allowed to slowly warm to room temperature and was stirred for 2 h. The reaction was quenched with 10 mL of brine and 20 mL of ether. The layers were separated, and the aqueous layer was extracted with ether (2 × 20 mL). The organic fractions were combined, dried over potassium carbonate, concentrated *in vacuo*, and chromatographed through 100 g of silica gel that was slurry packed with 100% hexane containing 1% triethylamine. The product was eluted with 100% hexane as a mixture of regioisomers. This mixture was treated with 25 mL of 3% HCl in methanol at 0 °C for 30 min to deprotect the alcohol. The reaction was quenched with 25 mL of saturated aqueous sodium bicarbonate and the aqueous fraction extracted with ether (3 × 25 mL). The organic fractions were combined, dried over potassium carbonate, concentrated *in vacuo*, and chromatographed through 100 g of silica gel that was slurry packed with a 10% ether/hexane solution containing 1% triethylamine. Gradient elution from 10% ether/hexane to 30% ether/hexane afforded 0.282 g (37%) of a 1.4:1 mixture of the desired product **39** and the other product regioisomer 5-methyl-6-(trimethylsilyl)-5-hexen-1-ol. An additional 0.160 g (22%) of the pure desired product was obtained as a 9:1 mixture of cis/trans isomers. The spectral data are as follows: ^1H NMR ($CDCl_3$/300 MHz) δ 5.99 (q, 0.9 H, *J* = 6.9 Hz), 5.81 (q, 0.1 H, *J* = 6.5 Hz), 3.57 (t, 2 H, 6.6 Hz), 2.11 (t, 0.2 H, *J* = 8.0 Hz), 2.01 (t, 1.8 H, *J* = 7.6 Hz), 1.69 (d, 2.7 H, *J* = 7.0 Hz), 1.63 (d, 0.3 H, *J* = 6.6 Hz), 1.6–1.45 (m, 2 H), 1.36–1.26 (m, 2 H), 0.10 (s, 8.1 H), 0.00 (s, 0.9 H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 141.9, 140.2, 136.9, 134.5, 62.7, 38.0, 32.8, 32.4, 28.7, 26.6, 25.7, 17.4, –0.23, –1.55; IR (neat/NaCl) 3333, 2934, 2860, 1616, 1448, 1249, 1055, 841 cm^{-1}; GC/MS (PCI) *m/e* (relative intensity) 187 (M^+ + 1, 6.7), 186 (M^+, 1.9), 185 (M^+ – 1, 5.4), 171 (M^+ – CH_3, 100), 169 (M^+ – OH, 13), 153 (65), 129 (27), 113 (M^+ – C_4H_9O, 6.9), 103 (28), 95 (98), 73 (87); HRMS (EI) *m/e* calcd for $C_9H_{19}OSi$ (M^+ – CH_3) 171.1205, found 171.1210.

(*E* and *Z*)-1-Methoxy-6-(trimethylsilyl)-1,6-octadiene (40). To a solution of 1.45 g (4.2 mmol) of (methoxymethyl)triphenylphosphonium chloride in 10 mL of THF at 0 °C was added 2.7 mL (4.6 mmol) of a 1.7 M *tert*-butyllithium in hexane solution. The dark-red reaction mixture was allowed to warm to room temperature and then stirred for 1 h. In a separate reaction flask 0.14 g (1.1 mmol) of oxalyl chloride was added to a stirred solution of 0.186 g (1.0 mmol) of (*E* and *Z*)-5-(trimethylsilyl)-5-hepten-1-ol and 0.094 g (1.2 mmol) of DMSO in 8 mL of THF at –25 °C. The reaction temperature was lowered to –60 °C and the reaction mixture stirred for 15 min. The reaction was quenched with 0.30 g (3 mmol) of triethylamine, the ice bath removed, and the reaction mixture stirred for 15 min at room temperature. The reaction was diluted with 10 mL of THF and filtered to remove the insoluble salts. The clear filtrate was then added to the ylide formed above at 0 °C. The reaction mixture was warmed to room temperature and stirred for 16 h. After this the reaction mixture was diluted with 10 mL of brine and 10 mL of ether. The layers were separated, and the aqueous layer was extracted with ether (2 × 10 mL). The organic fractions were combined, dried over potassium carbonate, and concentrated *in vacuo*. The crude product was chromatographed by dry-column flash chromatography through 75 g of silica gel with 100% hexane as the eluant to afford 0.124 g (59%) of the desired product **40**. The spectral data for the mixture of isomers are as follows: ^1H NMR ($CDCl_3$/300 MHz) δ 6.26 (d, 0.56 H, *J* = 12.6 Hz), 6.01 (q, 1 H, *J* = 6.8 Hz), 5.84 (d, 0.44 H, *J* = 6.3 Hz), 4.69 (dt, 0.56 H, J_d = 12.6 Hz, J_t = 7.3 Hz), 4.33 (app dt, 0.44 H, J_d = 6.3 Hz, J_t = 7.2 Hz), 3.55, 3.48 (two s, 3 H), 2.02, 2.00 (two br s, 3 H), 1.91–1.84 (m, 1 H), 1.72 (d, 2.6 H, *J* = 6.6 Hz), 1.65 (d, 0.4 H, *J* = 6.6 Hz), 1.32 (p, 2 H, *J* = 7.6 Hz), 0.12, 0.02 (two s, 9 H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 147.1, 147.0, 146.1, 146.0, 140.2, 140.1, 136.6, 136.5, 134.1, 106.9, 102.9, 59.4, 55.8, 38.1, 37.9, 32.0, 31.0, 30.9, 28.7, 28.1, 27.5, 23.6, 17.7, 0.1, –1.2; IR (neat/NaCl) 2929, 2855, 1655, 1249, 1111, 838 cm^{-1}; GC/MS (PCI) *m/e* (relative intensity) 2.13 (M^+ + 1, 14.7), 212 (M^+, 1.0), 198 (M^+ – CH_3, 12.5), 139 (M^+ – C_3H_9Si, 11.3), 109 (99), 89 (100), 81 (66), 73 (90). HRMS (EI) *m/e* calcd for $C_{12}H_{24}OSi$ 212.1596, found 212.1567.

Electrolysis of Compound 40. The electrolysis of compound **40** was done in a fashion similar to that for the electrolysis of compound **37**. In this reaction 0.211 g (1.0 mmol) of compound **40** in the presence of 0.50 g (4.7 mmol) of 2,6-lutidine was electrolyzed at a constant current of 23.4 mA until 192 C (2 F/mol) of charge had been passed. The reaction led to 0.088 g (52%) of a mixture of 2-methyl-2-cyclohexene-1-carboxaldehyde dimethyl acetal (**41**) and 2-methyl-3-cyclohexene-1-carboxaldehyde dimethyl acetal (**42**). Spectral data for the product mixture are as follows: ^1H NMR ($CDCl_3$/300 MHz) δ 5.64–5.58 (m, 1 H), 5.49–5.44 (m, 0.77 H), 4.32 (d, 0.23 H, *J* = 5.5 Hz), 4.26 (d, 0.54 H, *J* = 6.3 Hz), 4.16 (d, 0.23 H, *J* = 9.1 Hz), 3.37, 3.34, 3.33, 3.29 (four s, 6 H), 2.24–1.21 (m, 7 H, containing a doublet at 1.7 ppm, *J* = 2.1 Hz), 1.01 (d, 1.7 H, *J* = 7.0 Hz), 0.87 (d, 0.6 H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$/75 MHz) δ 133.3, 133.2, 132.5, 125.9, 125.7, 124.8, 107.5, 106.0, 105.4, 55.5, 54.3, 53.9, 52.4, 42.0, 41.3, 38.8, 30.5, 29.7, 25.6, 25.3, 23.2, 21.0, 20.0, 19.8, 18.8, 15.2; GC/MS (PCI) *m/e* (relative intensity) 171 (M^+ + 1, 47), 170 (M^+, 4.4), 169 (M^+ – 1, 21), 139 (M^+ – CH_3O, 100), 123 (15), 108 (M^+ – $C_2H_6O_2$, 98), 95 (M^+ – $C_3H_7O_2$, 10), 75 (84); HRMS (EI) *m/e* calcd for $C_9H_{15}O$ (M^+ – CH_3O) 139.1123, found 139.1163. At 500 MHz the resolution-enhanced ^1H NMR of the doublet at 1.7 ppm revealed a doublet of a quartet with J_d = 0.7 Hz and J_q = 2.0 Hz. Although not isolated from this mixture of products, a third product was tentatively assigned as 2-methyl-3-(trimethylsilyl)-3-cyclohexene-1-carboxaldehyde dimethyl acetal (**45**). This assignment was based on the ^1H NMR and GC/MS: ^1H NMR ($CDCl_3$/300 MHz) δ 5.96 (t, *J* = 3.48 Hz), 5.90 (t, *J* = 3.76 Hz), 0.03 (s); GC/MS (PCI) *m/e* (relative intensity) peak one 242 (M^+, 0.02), 241 (M^+ – 1, 0.40), 227 (M^+ – CH_3, 3.4), 211 (M^+ – CH_3O, 11), 196 (M^+ – C_2H_6O, 1.6), 107 (32), 75 (100), 73 (7.8); GC/MS (PCI) *m/e* (relative intensity) peak two 243 (M^+ + 1, 0.28), 241 (M^+, 0.79), 227 (M^+ – CH_3, 4.1), 211 (M^+ – CH_3O, 16), 196 (M^+ – C_2H_6O, 2), 107 (33), 75 (100), 73 (12). Based on the acetal protons in the ^1H NMR, the yield of this product was determined to be 6%.

(*E* and *Z*)-2-(Dimethyl-(2-methyl-1-propenyl)siloxy)-1-(methoxymethylidene)cyclohexane (48a). A solution of 0.68 g (2 mmol) of (methoxymethyl)triphenylphosphonium chloride in 4 mL of THF at 0 °C was treated with 1.2 mL (2 mmol) of 1.7 M *tert*-butyllithium in hexane. The resulting dark-red solution was allowed to stir for 1 h at room temperature. In a separate flask, a solution of 0.16 g (1.2 mmol)

of 1-bromo-2-methylpropene (**46a**) in 1 mL of THF at −78 °C was treated with 1.4 mL (2.4 mmol) of 1.7 M *tert*-butyllithium in hexane. The reaction mixture was allowed to warm to −40 °C over 30 min and then stirred for 1 h at −40 °C. The reaction temperature was decreased to −78 °C, and the reaction was quenched with 0.18 g (1.3 mmol) of freshly distilled (*N,N*-dimethylamino)dimethylchlorosilane. The reaction mixture was stirred an additional 10 min at −78 °C and then allowed to warm to room temperature over 30 min. A solution of 0.14 g (1.2 mmol) of 2-hydroxycyclohexanone in 1 mL of THF was added, and the reaction mixture was allowed to stir at room temperature for 4 h. The crude product **47a** was filtered through Florisil, concentrated *in vacuo*, and diluted with 2 mL of THF, and the resulting solution was added dropwise to a 0 °C solution of the ylide generated above. The resulting reaction mixture was allowed to warm to room temperature. After 16 h, the mixture was filtered through Florisil and concentrated *in vacuo*. Kugelrohr distillation (90 °C, 1 Torr) afforded 0.1 g (35%) of the desired product **48a**. The spectral data for **48a** are as follows: ^{1}H NMR (acetone-d_6/300 MHz) δ 5.96 (s, 0.58 H), 5.72 (d, 0.42 H, J = 1.8 Hz), 5.17 (s, 1 H), 4.86 (br, 0.42 H), 4.11 (t, 0.58 H, J = 4.6 Hz), 3.52, 3.51 (two s, 3 H), 2.27–2.14 (m, 2 H), 1.84, 1.824, 1.817, 1.83 (4s, 6 H), 1.79–1.15 (m, 6 H), 0.134, 0.129, 0.119 (three s, 6 H); ^{13}C NMR (acetone-d_6/75 MHz) δ 154.5, 154.0, 142.2, 141.1, 124.3, 123.9, 120.2, 120.1, 71.3, 63.9, 59.6, 37.6, 35.5, 29.5, 28.9, 27.2, 26.6, 23.5, 23.4, 23.0, 22.7, 21.2, 0.60, 0.44, 0.09; IR (neat/NaCl) 2931, 2855, 1684, 1622, 1447, 1249, 1131, 1084, 1039, 1014, 814 cm^{-1}; GC/MS (PCI) *m/e* (relative intensity) peak one 255 (M^+ + 1, 0.24), 254 (M^+, 0.21), 239 ($M^+ - CH_3$, 2.1), 223 ($M^+ - CH_3O$, 2.8), 199 ($M^+ - C_4H_7$, 5.3), 149 (3.2), 125 ($M^+ - C_6H_{13}OSi$, 92), 115 (57), 103 (11), 93 (38), 75 (100); GC/MS (PCI) *m/e* (relative intensity) peak two 255 (M^+ + 1, 0.19), 254 (M^+, 0.24), 239 ($M^+ - CH_3$, 1.7), 223 ($M^+ - CH_3O$, 4.1), 199 ($M^+ - C_4H_7$, 4.0), 149 (3.7), 125 ($M^+ - C_6H_{13}OSi$, 100), 115 (65), 103 (12), 93 (40), 75 (95); HRMS (EI) *m/e* calcd for $C_{14}H_{26}O_2Si$ 254.1702, found 254.1693.

Electrolysis of Compound 48a. Synthesis of *trans*-2-(Methoxydimethylsiloxy)-1-(2-methyl-1-propenyl)cyclohexanecarboxaldehyde Dimethyl Acetal (50) and *trans*-2-Hydroxy-1-(2-methyl-1-propenyl)cyclohexanecarboxaldehyde Dimethyl Acetal. A solution of 1.55 g of lithium perchlorate in 15 mL of methanol/THF (1:1) containing 0.128 g (0.50 mmol) of enol ether **48a** was placed in a three-neck round-bottom flask equipped with a nitrogen inlet, a reticulated vitreous carbon anode (suspended from a carbon rod), and a platinum-wire cathode. The mixture was degassed via sonication (5 min). The reaction mixture was cooled to 0 °C, 0.32 g (3.0 mmol) of 2,6-lutidine added, and the reaction electrolyzed at a constant current of 24 mA until 97 C (2 F/mol) of charge had been passed. The reaction was diluted with 15 mL of water, and the organic solvents were removed *in vacuo*. The aqueous fraction was extracted with ether (3 × 20 mL), dried over potassium carbonate, concentrated *in vacuo*, and distilled with the use of a Kugelrohr apparatus (115 °C at 1 Torr) to afford 0.114 g (72%) of the desired product as a single isomer. The spectral data are as follows: ^{1}H NMR (acetone-d_6/300 MHz) δ 5.34 (s, 1 H), 4.17 (s, 1 H), 3.80 (dd, 1 H, J_1 = 11.1 Hz, J_2 = 3.9 Hz), 3.45, 3.41, 3.36 (three s, 9 H), 2.30–2.26 (m, 1 H), 1.77, 1.76 (two s, 6 H), 1.86–1.21 (m, 7 H); ^{13}C NMR (acetone-d_6/75 MHz) δ 135.7, 123.3, 110.2, 75.8, 60.0, 56.4, 52.4, 50.1, 32.4, 29.3, 26.3, 25.5, 21.7, 19.6, −2.9, −3.1; IR (neat/NaCl) 2937, 2860, 2832, 1456, 1102, 1256, 903, 848, 798 cm^{-1}; GC/MS (PCI) *m/e* (relative intensity) 316 (M^+, 0.16), 315 ($M^+ - 1$, 0.34), 301 ($M^+ - CH_3$, 0.26), 285 ($M^+ - CH_3O$, 1.5), 270 ($M^+ - C_2H_6O$, 0.23), 179 (9.8), 165 (18), 149 (100), 99 (99), 85 (34). Although not evident by NMR, the GC trace of the distilled material revealed the presence of approximately 4% of the deprotected alcohol. This product was characterized by treatment of the mixture with 2 mL of 1 M tetrabutylammonium fluoride in THF at room temperature for 30 min. The reaction was diluted with 10 mL of water and 15 mL of ether. The layers were separated, and the aqueous layer was extracted with ether (2 × 15 mL). All organic fractions were combined, dried over potassium carbonate, concentrated *in vacuo*, and chromatographed through 60 mL of basic alumina (activity III) with a gradient elution from 10% ether/hexane to 30% ether/hexane. The yield over the two-step process (oxidation and deprotection) was 53%. The spectral data for the alcohol are as follows: ^{1}H NMR (acetone-d_6/300 MHz) δ 5.37 (s, 1 H), 4.36 (s, 1 H), 3.70 (d with fine coupling, 1 H, J = 12 Hz), 3.59 (d, 1 H, J = 2.0 Hz), 3.44, 3.43 (two s, 6 H), 2.15 (d with fine coupling, 1 H, J = 8.8 Hz), 1.76, 1.75 (two s, 6 H), 1.56 (d, 2 H, J = 9 Hz), 1.43–1.13 (m, 5 H); ^{13}C NMR (acetone-d_6/75 MHz) δ 135.9, 124.6, 114.0, 74.5, 60.0, 59.4, 52.3, 32.5, 30.2, 26.5, 23.1, 21.1; IR (neat/NaCl) 3503, 2934, 2859, 1457, 1068 cm^{-1}; GC/MS (PCI) *m/e* (relative intensity) 229 (M^+ + 1, 0.12), 211 (M^+ − OH, 0.24), 197 ($M^+ - CH_3O$, 22), 180 ($M^+ - CH_4O_2$, 1.7), 165 (27), 147 (47), 121 (15), 99 (100), 81 (45); HRMS (EI) *m/e* calcd for $C_{12}H_{21}O_2$ ($M^+ - CH_3O$) 197.1531, found 197.1541.

***trans*-2-Hydroxy-1-(2-methyl-1-propenyl)cyclohexanecarboxaldehyde (51) and *cis*-2-Hydroxy-1-(2-methyl-1-propenyl)cyclohexanecarboxaldehyde (52).** Treatment of the crude product from the electrochemical oxidation of **48a** with an HCl/water/methanol solution (ratio = 1.5:1.5:47, respectively) at 0 °C for 15 min resulted in the formation of alcohol aldehyde **51** as a single isomer. The spectral data for **51** are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 9.60 (s, 1 H), 5.24 (d, 1 H, J = 1.3 Hz), 3.99 (dd, 1 H, J_1 = 9.2 Hz, J_2 = 3.8 Hz), 2.1 (br s, 1 H), 1.97–1.91 (m, 1 H), 1.84 (s, 3 H), 1.81–1.66 (m, 2 H), 1.64 (s, 3 H), 1.60–1.26 (m, 5 H); ^{13}C NMR ($CDCl_3$/75 MHz) δ 205.0, 139.4, 120.1, 71.7, 56.5, 30.0, 29.9, 27.4, 22.7, 20.9, 19.6; IR (neat/NaCl) 3325, 2934, 2859, 1717, 1456 cm^{-1}; GC/MS (PCI) *m/e* (relative intensity) 183 (M^+ + 1, 100), 182 (M^+, 1.7), 165 (M^+ − OH, 24), 97 (7.4). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.5; H, 9.89. Found: C, 72.0; H, 9.92. When the crude product from the electrochemical oxidation of **48a** was washed with 0.5 N HCl during workup, alcohol aldehyde isomers **51** and **52** were obtained. The spectral data for the mixture of isomers **51** and **52** are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 9.56 (s, 0.6 H), 9.38 (s, 0.4 H), 5.21 (s, 0.6), 5.09 (s, 0.4 H), 4.06 (br s, 0.4 H), 3.96 (dd, 0.6 H, J_1 = 9.1 Hz, J_2 = 3.6 Hz), 1.96–1.84 (m, 1 H), 1.81 (d, 1.8 H, J = 1.3 Hz), 1.76 (d, 1.2 H, J = 1.5 Hz), 1.75–1.63 (m, 2 H), 1.61 (s, 1.8 H), 1.56 (s, 1.2 H), 1.55–1.29 (m, 5 H). Irradiation of the vinyl proton at 5.21 ppm (corresponding to product **51**) resulted in an NOE of <0.05% for the proton located α to the hydroxyl group (3.96 ppm). Irradiation of the vinyl proton at 5.09 ppm (corresponding to product **52**) resulted in an NOE of 1.01% for the proton located α to the hydroxyl group (4.06 ppm): ^{13}C NMR ($CDCl_3$/75 MHz) δ 204.7, 204.4, 139.3, 138.8, 121.8, 120.0, 71.7, 70.7, 56.6, 55.1, 30.2, 30.0, 29.7, 29.3, 27.6, 27.4, 22.9, 21.1, 20.8, 20.2, 19.9, 19.3; GC/MS (PCI) *m/e* (relative intensity) 183 (M^+ + 1, 24), 182 (M^+, 3.8), 165 (M^+ − OH, 100), 97 (18).

***(E* and *Z)*-2-(Dimethyl-1-propenylsiloxy)-1-(methoxymethylidene)cyclohexane (48b).** A solution of 1.38 g (4 mmol) of (methoxymethyl)triphenylphosphonium chloride in 8 mL of THF at 0 °C was treated with 2.7 mL (4.0 mmol) of 1.5 M *tert*-butyllithium in hexane. The resulting dark-red solution was allowed to stir for 1 h at room temperature. In a separate flask a solution of 0.36 g (3.0 mmol) of 1-bromopropene (**46b**) in 6 mL of THF at −78 °C was treated with 4.0 mL (6.0 mmol) of 1.5 M *tert*-butyllithium in hexane. The reaction mixture was allowed to warm to −40 °C over 30 min and then stirred for 1 h at −40 °C. The reaction temperature was decreased to −78 °C, and the reaction was quenched with 0.41 g (3.0 mmol) of freshly distilled (*N,N*-dimethylamino)-dimethylchlorosilane. The reaction mixture was stirred an additional 10 min at −78 °C and then allowed to warm to room temperature over 1 h. A solution of 0.35 g (3.5 mmol) of 2-hydroxycyclohexanone in 12 mL of THF was added. The reaction was heated to reflux for 3 h. After cooling, the crude product **47b** was filtered through Florisil, concentrated *in vacuo*, and diluted with 6 mL of THF, and the resulting solution was added dropwise to a 0 °C solution of the ylide generated above. The resulting reaction mixture was allowed to warm to room temperature. After 16 h, the mixture was filtered through Florisil and concentrated *in vacuo*. Kugelrohr distillation (100 °C, 1 Torr) followed by chromatography through silanized silica gel with 100% hexane as the eluant afforded 0.219 g (30%) of the desired product **48b**. The spectral data for **48b** are as follows: ^{1}H NMR (acetone-d_6/300 MHz) δ 6.50–6.34 (m, 0.6 H), 6.25–6.12 (m, 0.4 H), 5.99, 5.97 (two s, 0.67 H), 5.72, 5.73 (two s, 0.33 H), 5.66 (d, 0.4 H, J = 18.5 Hz), 5.47, 5.46 (two d, 0.6 H, J = 14.2 Hz), 4.87 (d, 0.3 H, J = 9.3 Hz), 4.15–4.08 (m, 0.7 H), 3.52, 3.51 (two s, 3 H), 2.25–2.11 (m, 2 H), 1.84–1.70 (m, 4 H), 1.60–1.27 (m, 5 H), 0.17, 0.15, 0.10, 0.09, 0.08, (five s, 6H); ^{13}C NMR (acetone-d_6/75 MHz) δ 145.8, 145.2, 144.8, 144.2, 142.3, 142.2, 141.2, 131.4, 131.1, 129.8, 129.5, 120.0, 71.4, 71.3, 64.1, 64.0, 59.6, 37.7, 37.6, 35.5, 28.9, 27.2, 26.6, 23.1, 23.0, 22.8, 22.7, 22.6, 21.2, 21.1, 19.5, 19.4, 0,68, 0.53, 0.16, −0.97, −1.05, −1.14, −1.35; IR (neat/NaCl) 2932, 2855, 1686, 1620, 1446, 1250, 1132, 1014, 900 cm^{-1}; GC/MS (PCI) *m/e* (relative intensity) peak one 240 (M^+, 4.4), 225 ($M^+ - CH_3$, 30), 209 ($M^+ - CH_3O$, 5.4), 199 ($M^+ - C_3H_5$, 37), 125 ($M^+ - C_5H_{11}Si$, 100), 99 (11), 75 (12); GC/MS (PCI) *m/e* (relative intensity) peak two 240 (M^+, 3.3), 225 ($M^+ - CH_3$, 20), 209 ($M^+ - CH_3O$, 11), 199 ($M^+ - C_3H_5$, 33), 125 ($M^+ - C_5H_{11}Si$, 100), 99 (14), 75 (20); GC/MS (PCI) *m/e* (relative intensity) peak three 240 (M^+, 4.9), 225 ($M^+ - CH_3$, 24), 209 ($M^+ - CH_3O$, 26), 199 ($M^+ - C_3H_5$, 42), 125 ($M^+ - C_5H_{11}Si$, 100), 99 (26), 75 (26); GC/MS (PCI) *m/e* (relative intensity) peak four 240 (M^+, 2.7), 225 ($M^+ - CH_3$, 13), 209 ($M^+ - CH_3O$, 17), 199 ($M^+ - C_3H_5$, 27), 125 (M^+ −

$C_5H_{11}Si$, 100), 99 (44), 75 (69); HRMS (E/I) *m/e* calcd for $C_{13}H_{24}O_2Si$ 241.1545, found 240.1544.

Electrolysis of Compound 48b. Synthesis of (*E* and *Z*)-*trans*-2-Hydroxy-1-(1-propenyl)cyclohexanecarboxaldehyde Dimethyl Acetal (57). A solution of 1.89 g of lithium perchlorate in 45 mL of methanol/dichloromethane (1:4) containing 0.092 g (0.38 mmol) of enol ether **48b** was placed in a three neck round bottom flask equipped with a nitrogen inlet, a reticulated vitreous carbon anode (suspended from a carbon rod), and a platinum-wire cathode. The mixture was degassed via sonication (5 min), and 0.13 g (1.2 mmol) of 2,6-lutidine was added. The reaction was electrolyzed at a constant current of 14.2 mA until 73 C (2 F/mol) of charge had been passed. The reaction mixture was diluted with 25 mL of water, the layers were separated, and the aqueous layer was extracted with dichloromethane (2 × 25 mL). The organic fractions were combined and concentrated *in vacuo*. At this point, an NMR yield indicated that product **56** was formed in an approximate 33% yield. Product **56** could not be isolated without loss of the silyl group, so the crude product was treated with 2 mL of a 1 M solution of tetrabutylammonium fluoride in THF for 30 min at room temperature. The reaction mixture was diluted with 5 mL of ether and washed with 0.5 N HCl (2 × 3 mL). All aqueous fractions were combined, extracted with ether (3 × 5 mL), dried over potassium carbonate, concentrated *in vacuo*, and chromatographed through 20 g of silica gel with a gradient elution from 20% ether/hexane to 40% ether/hexane as the eluant to afford 0.026 g (31%) of the desilated product **57**. A 50:1 ratio of olefin isomers was obtained. The spectral data are as follows: ^{1}H NMR (acetone-d_6/300 MHz) δ 5.63–5.60 (m, 2 H), 4.36 (s, 0.02 H), 4.15 (s, 0.98 H), 3.74 (ddd, 1 H, J = 9.9, 4.5, 2.5 Hz), 3.51 (d, 1 H, J = 2.3 Hz), 3.45 and 3.41 (two s, 6 H), 1.78–1.74 (m, 1 H), 1.71 (d, 3 H, J = 4.9 Hz), 1.61–1.53, (m, 2 H), 1.39–1.29 (m, 5 H); ^{13}C NMR of the major isomer (acetone-d_6/75 MHz) δ 130.4, 127.2, 113.4, 72.4, 58.7, 58.3, 50.4, 31.4, 28.7, 25.3, 21.5, 19.0; IR (neat/NaCl) 3463, 2935, 2862, 1456, 1069, 977; GC/MS (PCI) *m/e* (relative intensity) 214 (M^+, 2.5), 183 ($M^+ - CH_3O$, 18), 151 ($M^+ - C_2H_7O_2$, 20), 139 ($M^+ - C_3H_7O_2$, 16), 125 (20), 85 (51), 75 (66), 61 (100); HRMS (EI) *m/e* calcd for $C_{11}H_{18}O_2$ ($M^+ - CH_3O$) 182.1306, found 182.1311.

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Supplementary Material Available: Proton and carbon NMR data for all new compounds, HMQC and HMQC-TOCSY spectrum for compound **44b**, and NOE difference spectra for **51** and **52** (57 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.