Intramolecular Anodic Olefin Coupling Reactions: A New Approach to the Synthesis of Angularly Fused, Tricyclic Enones[1]

Luzviminda V. Tinao-Wooldridge, Kevin D. Moeller,* and Christine M. Hudson†

Department of Chemistry, Washington University, St. Louis, Missouri 63130

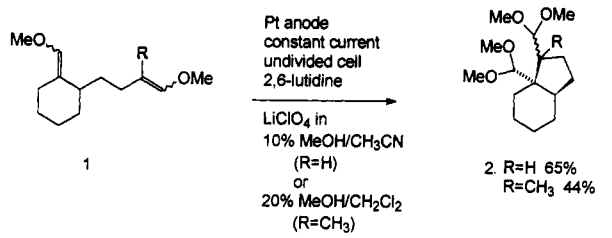
Received January 12, 1994®

A number of intramolecular anodic olefin coupling reactions have been examined in order to determine the feasibility of using a sequential electrochemical oxidation–aldol condensation approach for constructing polycyclic enones. Initially, substrates comprised of an aldehyde enol ether tethered to a ketone enol ether were examined. In a model study, it was shown that such a substrate could lead to a successful electrochemical oxidation–aldol condensation sequence. However, the difficulties associated with both the synthesis and the poor stability of the ketone enol ethers greatly reduced the potential utility of this approach. This problem was circumvented by taking advantage of the compatibility of allylsilane groups with the electrolysis reaction. In these examples, ozonolysis of the electrochemical cyclization product afforded the 1,4-dicarbonyl substrate needed for the aldol condensation. The use of the less reactive allylsilane group in the electrochemical reaction still allowed for the construction of quaternary carbons. Finally a pair of angularly fused, tricyclic enones were synthesized. The regiochemistry of the enone in the product could be controlled by the proper choice of the substrate for the electrolysis and manipulation of the resulting cyclized product.

Recently, we reported that the intramolecular anodic coupling of enol ethers could lead to the formation of quaternary carbons with control of relative stereochemistry (Scheme 1).[2] These reactions were intriguing because they served to illustrate the reactivity of the radical-cation intermediates formed during the electrolysis reaction, led to the construction of fused bicylic ring skeletons, and generated potentially useful 1,4-dicarbonyl equivalents. For example, if the enol ether of a ketone were compatible with the anodic oxidation reactions, then the electrolysis reactions could, in principle, be followed by an intramolecular aldol condensation in order to assemble the angularly-fused tricyclic ring skeletons found in a number of important natural products like retigeranic acid,[3] crinipellin A,[4] and magellanine (Scheme 2).[5] All three of these natural products have been synthesized with the use of either an angularly fused tricyclic enone or ketone building block.[6]

In order to test the viability of using a sequential electrochemical oxidation–aldol condensation sequence for

Scheme 1



synthesizing polycyclic enones, substrate 8 was synthesized and oxidized. The synthesis of 8 is outlined in Scheme 3.[7] Compound 8 proved to be difficult to isolate because of its propensity to hydrolyze to the corresponding ketone. Consequently, the overall yield of this process was disappointing. Once isolated, however, substrate 8 could be readily oxidized at a constant current of 15 mA in an undivided cell using a platinum gauze anode, a carbon rod auxiliary electrode, 2,6-lutidine as a proton scavenger, and a 0.5 M lithium perchlorate in 10% methanol/THF electrolyte solution (Scheme 4). Current was passed until there was no starting material detected by TLC (2.0 F/mol). The ^{1}H NMR of the crude electrolysis mixture indicated that a mixture of cyclized products had been formed. Past cyclizations of bis enol ethers have led to a mixture of cyclic and acyclic acetals.[2] In order to simplify isolation of the products, the number of products was reduced by treatment of the crude reaction mixture with *p*-toluene-

† In part.

® Abstract published in *Advance ACS Abstracts,* April 1, 1994.

(1) Taken in part from: Tinao-Wooldridge, L. V. Ph.D. Thesis, Washington University, St. Louis, MO, 1993.

(2) Moeller, K. D.; Tinao, L. V. *J. Am. Chem. Soc.* **1992**, *114*, 1033.

(3) (a) Kaneda, M.; Takahashi, R.; Iitaka, Y.; Shibata, S. *Tetrahedron Lett.* **1972**, 4609. (b) Kaneda, M.; Iitaka, Y.; Shibata, S. *Acta Cryst.* **1974**, *B30*, 358. (c) Hans, J. R. *Nat. Prod. Rep.* **1986**, *3*, 123. For syntheses, see: (d) Wender, P. A.; Singh, S. K. *Tetrahedron Lett.* **1990**, *31*, 2517. (e) Hudlicky, T.; Fleming, A.; Radesca, L. *J. Am. Chem. Soc.* **1989**, *111*, 6691. (f) Wright, J.; Drtina, G. J.; Roberts, R. A.; Paquette, L. A. *J. Am. Chem. Soc.* **1988**, *110*, 5806. (g) Hudlicky, T.; Radesca-Kwart, L.; Li, L.; Bryant, T. *Tetrahedron Lett.* **1988**, 3283. (h) Paquette, L. A.; Wright, J.; Drtina, G.; Roberts, R. A. *J. Org. Chem.* **1987**, *52*, 2960. (i) Corey, E. J.; Desai, M. C.; Engler, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 4339.

(4) (a) Anke, T.; Heim, J.; Knoch, F.; Mocek, U.; Steffan, B.; Steglich, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 109. (b) Kupka, J.; Anke, T.; Oberwinkler, F.; Schramm, G.; Steglich, W. *J. Antibiot.* **1979**, *32*, 130. (c) Piers, E.; Renaud, J. *J. Org. Chem.* **1993**, *25*, 11–13. For prior synthetic efforts, see: (d) Curran, D. P.; Sisko, J. Yeske, P. E.; Liu, H. *Pure Appl. Chem.* **1993**, *65*, 1153. (e) Mehta, G.; Rao, K. S.; Reddy, M. S. *J. Chem. Soc., Perkin Trans. 1* **1991**, 693. (f) Schwartz, C. E.; Curran, D. P. *J. Am. Chem. Soc.* **1990**, *112*, 9272. (g) Mehta, G.; Rao, K. S.; Reddy, M. S. *Tetrahedron Lett.* **1988**, *29*, 5025. (h) Mehta, G.; Rao, K. S. *J. Chem. Soc., Chem. Commun.* **1987**, 1578.

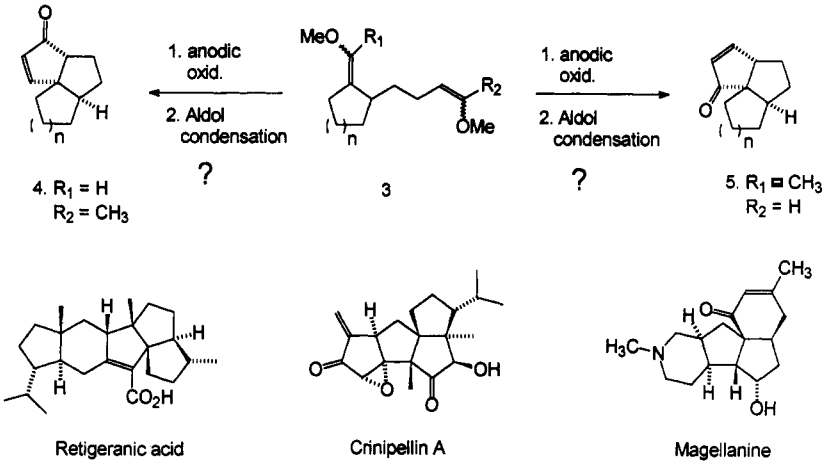
(5) (a) Loyola, L. A.; Morales, G.; Castillo, M. *Phytochemistry* **1979**, *18*, 1721. (b) Castillo, M.; Loyola, L. A.; Morales, G.; Singh, I.; Calvo, C.; Holland, H. L.; Maclean, D. B. *Can. J. Chem.* **1976**, *54*, 2893. For total syntheses, see: (c) Paquette, L. A.; Friedrich, D.; Pinard, E.; Williams, J. P.; St. Laurent, D.; Roden, B. A. *J. Am. Chem. Soc.* **1993**, *115*, 4377. (d) Hirst, G. C.; Johnson, T. O., Jr.; Overman, L. E. *J. Am. Chem. Soc.* **1993**, *115*, 2992. For a previous approach to the ring skeleton, see: (e) Mehta, G.; Reddy, M. S. *Tetrahedron Lett.* **1990**, *31*, 2039.

(6) For examples, see ref 4f for retigeranic acid, ref 5c for crinipellin, and ref 6c for magellanane.

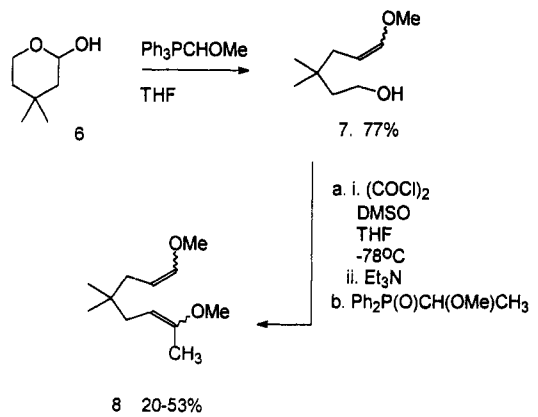
(7) For the use of (methoxyethyl)diphenylphosphine oxide, see: (a) Avery, M.; Jennings-White, C.; Chong, W. *J. Org. Chem.* **1989**, *54*(8), 1792. (b) Warren, S.; Earnshaw, C.; Wallis, C. *J. Chem. Soc. Perkin Trans. I* **1979**, 2099. (c) Heissler, D.; Ladenburger, C. *Tetrahedron* **1988**, *44*(9), 2513.

0022-3263/94/1959-2381$04.50/0

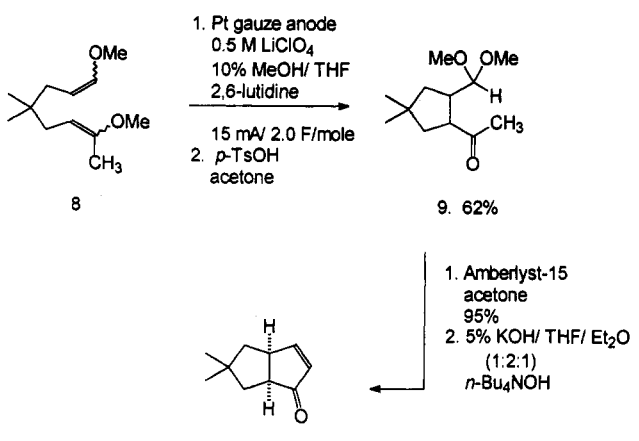
Scheme 2



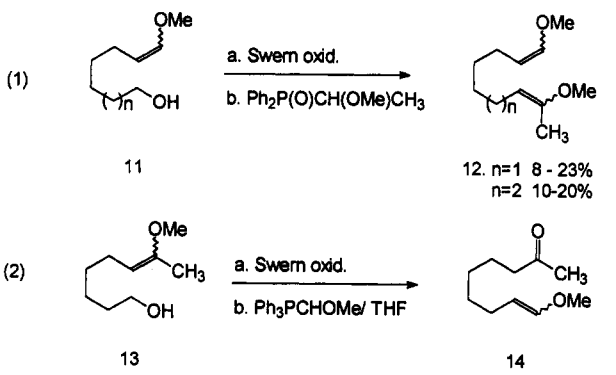
Scheme 3



Scheme 4



Scheme 5



sulfonic acid in acetone. A 62% isolated yield of the cyclized, monoprotected keto acetals **9** was obtained over the two steps as a mixture of cis and trans isomers. The acetal was deprotected with the use of Amberlyst-15 ion exchange resin and the aldol condensation completed by treatment of the resulting keto aldehyde with a 1:2:1 solution of 5% KOH in water/THF/ether and tetra-*n*-butylammonium hydroxide as a phase-transfer catalyst.[8] The desired bicyclic enone **10** was formed in 64% yield over the final two steps as a single (presumed cis)[9] isomer.

Although the formation of the bicyclic enone **10** was encouraging, the difficulties associated with the synthesis of the bis enol ether substrate did not bode well for the overall utility of the sequence. In fact, when the synthesis of compound **8** was "scaled up", the yield for the Horner–Emmons–Wadsworth reaction was most often closer to the 20% end of the range given in Scheme 3. The Horner–Emmons–Wadsworth reaction to make the ketone enol ether became even more troublesome with other substrates. For example, yields were typically in the 10–20% range for substrates that would lead to six- and seven-membered rings during the electrolysis (Scheme 5, eq 1). The problems with the synthesis could not be solved by reversing the order in which the enol ethers were introduced. This route (Scheme 5, eq 2) was continually plagued by hydrolysis of the trisubstituted enol ether. The synthesis of a substrate like **3** (n = 1, R_1 = H, R_2 = CH_3) for construction of a tricyclic enone with a central quaternary carbon proved impossible.

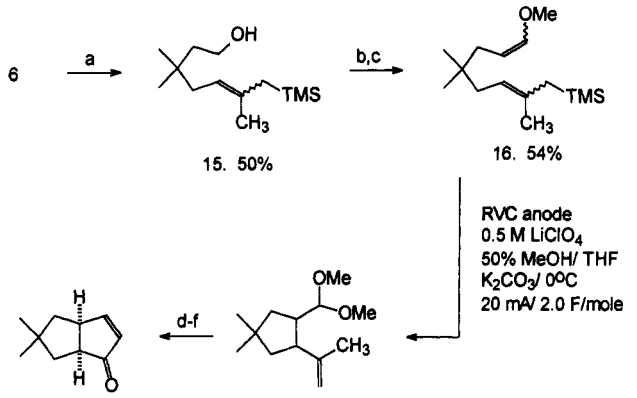
These difficulties caused us to consider alternative ketone surrogates for use in the anodic olefin coupling reaction–aldol condensation sequence. For example, allylsilane groups had proven to be excellent participants in the olefin coupling reactions and had led to the formation of olefin products with control of regiochemistry.[10] In principle, ozonolysis of the resulting olefin would give rise

(8) (a) Paquette, L. A.; Stevens, K. E. *Tetrahedron Lett.* **1981**, *22*(44), 4393. (b) Steinbach, D.; Ensinger, C. *J. Org. Chem.* **1990**, *55*, 2723. (c) Cohen, T.; Cherkauskas, J. *J. Org. Chem.* **1992**, *57*(1), 6.

(9) For comparison, cis-fused bicyclo[3.3.0]octane is approximately 7 kcal/mol less stable than trans-fused bicyclo[3.3.0]octane. (a) Chang, S.-J.; McNally, D.; Shary-Tehrany, S.; Hickey, M. J.; Boyd, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3109. (b) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982.

(10) (a) Moeller, K. D.; Hudson, C. H. *Tetrahedron Lett.* **1991**, *32*, 2307. (b) Hudson, C. H.; Marzabadi, M. R.; Moeller, K. D.; New, D. G. *J. Am. Chem. Soc.* **1991**, *113*, 7372.

Scheme 6[a]



[a] Reagents: (a) i, Ph_3PEtBr, *n*-BuLi, THF, 0 °C to rt; ii, ICH_2SiMe_3, 0 °C to rt; iii, *n*-BuLi, −78 °C to rt; (b) i, $(COCl)_2$, DMSO, THF, −78 °C; ii, Et_3N, −78 °C to rt; (c) Ph_3PCH_2OMe, THF, *t*-BuLi, −78 °C to rt; (d) i, O_3, 20% CH_2Cl_2/MeOH, −78 °C; ii, Zn/glacial HOAc, −78 °C to rt; (e) Amberlyst-15, 1.5% H_2O/acetone; (c) 5% aqueous KOH/ THF/Et_2O (1:2:1), cat. *n*-Bu_4NOH, reflux.

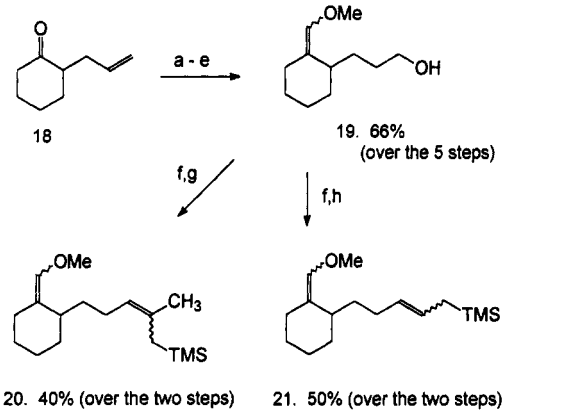
to a 1,4-dicarbonyl equivalent for the subsequent aldol condensation. The feasibility of such an approach was examined with the use of substrate **16** (Scheme 6). The synthesis of **16** was accomplished using a route identical to that reported earlier for the substrate without the *gem*-methyl groups.[10] Compound **16** was oxidized at 0 °C using a constant current of 20 mA (2.0 F/mol), a reticulated vitreous carbon (RVC) anode, a carbon rod auxiliary electrode, potassium carbonate as a proton scavenger, and a 0.5 M lithium perchlorate in 50% methanol/THF electrolyte solution. An 89% isolated yield of the cyclized product **17** was obtained as a mixture of cis and trans isomers. As a sidenote, the yield for this cyclization reaction was 23% higher than that obtained earlier for the substrate without the *gem*-methyl groups. The tandem sequence was completed by ozonolysis of compound **17**, cleavage of the acetal using Amberlyst-15, and then cyclization of the resulting 1,4-dicarbonyl equivalent with a 1:2:1 solution of 5% aqueous KOH/THF/ether and tetra-*n*-butylammonium hydroxide as a phase-transfer catalyst. A 52% yield of the desired bicyclic enone **10** was obtained over the three steps.

The success of this sequence and the relative ease with which the substrate could be made suggested that allylsilanes might function well for the construction of angularly fused tricyclic enones. However, previous cyclizations using allylsilanes as coupling participants had shown that allylsilanes were not as efficient as cyclization terminators as were enol ethers. Coupling reactions utilizing allylsilane participants *required* the use of cosolvents such as THF and dichloromethane, even when the cyclizations led to the formation of five- and six-membered rings.[10b] Similar cyclizations involving the coupling of bis enol ether substrates could be carried out in pure methanol solvent.[2] Would the use of the less reactive allylsilane group still allow for the construction of a quaternary carbon?[11]

In order to address this issue, two substrates were prepared as outlined in Scheme 7. Substrate **20** was oxidized at 0 °C using a constant current of 25 mA (2.1 F/mol), a RVC anode, a carbon rod cathode, potassium carbonate as a proton scavenger, and a 0.5 M lithium

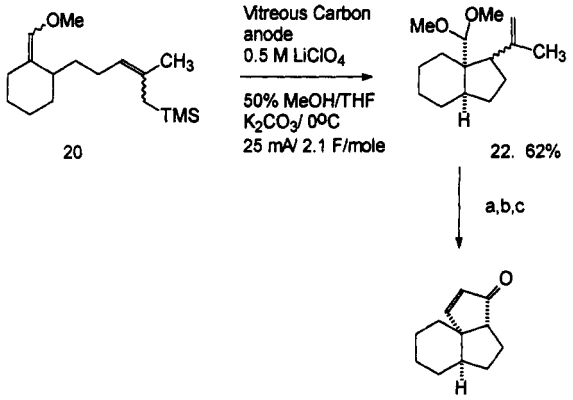
(11) For a preliminary account of this work, see: Moeller, K. D.; Hudson C. M.; Tinao-Wooldridge, L. V. *J. Org. Chem.* **1993**, *58*, 3478.

Scheme 7[a]



[a] Reagents: (a) $(CH_3O)_3CH$, K-10 Montmorillonite clay; (b) i, borane–methyl sulfide, 2-methyl-2-butene, THF, 0 °C; ii, NaOH, H_2O_2; (c) TBDPhSiCl, imidazole, DMF; (d) $Ph_3PCHOCH_3$, THF, 0 °C; (e) TBAF, THF; (f) i, $(COCl)_2$, DMSO, −40 °C; ii, Et_3N; (g) i, Ph_3PEtBr, *n*-BuLi, THF, 0 °C to rt; ii, ICH_2SiMe_3, 0 °C to rt; iii, *n*-BuLi , −78 °C to rt; (h) Ph_3PCHCH_2TMS, THF, −78 °C.

Scheme 8[a]

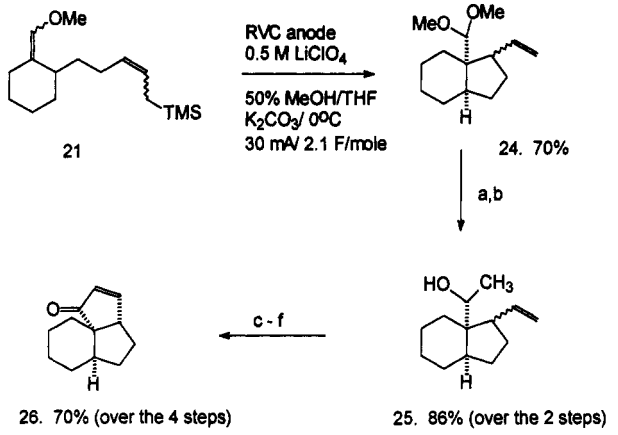


[a] Reagents: (a) i, O_3, 20% CH_2Cl_2/MeOH, −78 °C; ii, Zn, glacial HOAc, −78 °C to rt; (b) Amberlyst-15 ion-exchange resin, 1.5% H_2O/ acetone; (c) 5% aqueous KOH/THF/Et_2O (1:2:1), cat. *n*-Bu_4NOH, reflux.

perchlorate in 50% methanol/THF electrolyte solution. A 62% yield of the cyclized product **22** was isolated as a mixture of isomers about the newly formed carbon–carbon bond. As in earlier cyclization reactions, only cis isomers about the ring juncture were produced (Scheme 8). Compound **22** was converted to a substrate for the aldol condensation by ozonolysis of the double bond followed by hydrolysis of the resulting product with Amberlyst-15. The aldol condensation was again effected with the use of a 1:2:1 mixture of 5% KOH/THF/ether and a catalytic amount of the phase-transfer catalyst tetra-*n*-butylammonium hydroxide. A 68% isolated yield of the tricyclic enone product **23** was obtained over the three-step sequence as a single diastereoisomer. Presumably, the cis-fused thermodynamic product was formed.

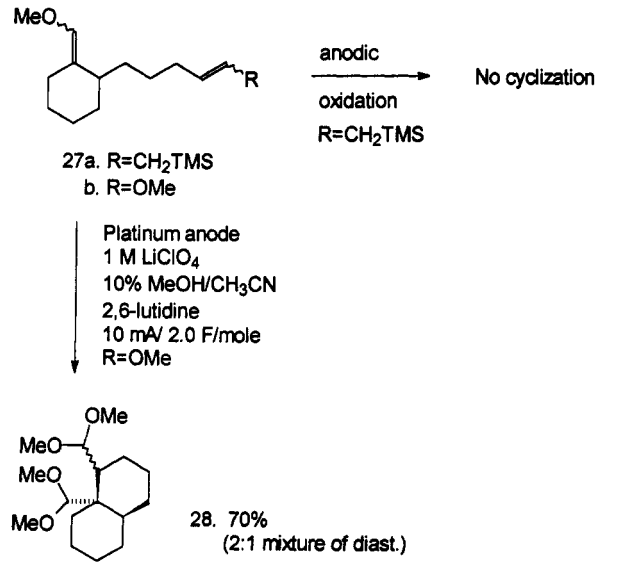
The complementary tricyclic enone was synthesized starting from substrate **21**. The electrolysis reaction was conducted under nearly identical conditions (30 mA, 2.1 F/mol) to the oxidation of **20** and afforded a 70% isolated yield of **24** (Scheme 9). Product **24** was again obtained as a mixture of two isomers. The acetal was cleaved with the use of Amberlyst-15 and the aldehyde treated with methylmagnesium bromide to form **25**. Swern oxidation

Scheme 9[a]



[a] Reagents: (a) Amberlyst-15, 1.5% H_2O/acetone; (b) i, MeMgBr, THF; ii, H_2O; (c) i, $(COCl)_2$, DMSO, THF, −78 °C; ii, Et_3N, −78 °C to rt; (d) i, O_3, 20% CH_2Cl_2/MeOH, −78 °C; ii,. Zn, glacial HOAc, −78 °C to rt; (e) Amberlyst-15, 1.5% H_2O/acetone; (f) 5% aqueous KOH/THF/Et_2O (1:2:1), cat. n-Bu_4NOH, reflux.

Scheme 10



of **25**, ozonolysis of the monosubstituted olefin, and hydrolysis of the resulting acetals generated during the ozonolysis led to the formation of a substrate for the aldol condensation. The aldol condensation afforded the desired tricyclic enone **26** in a 70% isolated yield over the four steps from **25**. As with the synthesis of **23**, only a single isomer of the tricyclic enone was obtained.

These two sequences demonstrate that anodic olefin coupling reactions leading to the formation of quaternary carbons and five-membered rings are compatible with the use of less reactive allylsilane participants. However, it is important to note that attempts to form a fused six-membered ring using chemistry directly analogous to the oxidation of **21** met with failure (Scheme 10).[12] In this case, the oxidation of **27a** did not lead to to the formation of any cycliczed product. For comparison, the analogous bis enol ether coupling reaction (**27b**) led to the formation of a 70% yield of cyclized product.[12] Clearly, the less facile olefin coupling reactions using allylsilanes can be pushed to a point where they fail to yield cyclized products.

In conclusion, the use of allylsilanes as participants in the anodic olefin coupling reactions allowed for the use of an electrochemical cyclization–aldol condensation sequence for the construction of both bicyclic and angularly fused tricyclic enones. The regiochemistry of the enone in the product could be controlled by the proper choice of the substrate for the electrolysis and manipulation of the resulting cyclized product. Studies aimed at determining the generality of this sequence and assessing its applicability to the synthesis of natural products are currently underway and will be reported in due course.

Experimental Section[13]

1,7-Dimethoxy-4,4-dimethyl-(*E,Z*)-1,6-octadiene (8). To a −78 °C solution of 0.34 mL (2.6 mmol) of diisopropylamine in 5.2 mL of THF was added 1.04 mL (2.6 mmol) of a 2.5 M n-butyllithium in hexane solution. The reaction was warmed to 0 °C over a period of 30 min. The reaction mixture was then slowly cannulated into a −78 °C solution of 0.754 g (2.9 mmol) of (methoxyethyl)diphenylphosphine oxide in 7.25 mL of THF. The deep red reaction mixture was kept from −78 °C to −40 °C for 3 h. In another flask, 0.158 g (1 mmol) of 3,3-dimethyl-6-methoxy-(*E,Z*)-5-hexen-1-ol[2] and 0.09 mL (1.3 mmol) of dimethyl sulfoxide in 3 mL of THF at −78 °C were treated with 0.11 mL (1.2 mmol) of oxalyl chloride. The reaction was allowed to stir for 20 min at −78 °C after which 0.42 mL (3 mmol) of triethylamine was added. After 5 min at −78 °C, the reaction was warmed to room temperature by adding THF to the reaction and removing the cold bath. The white solids were removed by filtration and the residue washed with THF. The combined filtrates were concentrated *in vacuo*, diluted with 5 mL of THF, and cannulated into the stirring −78 °C (methoxyethyl)diphenylphosphine oxide anion solution generated above. The reaction was kept at −78 °C for another hour and then allowed to warm to room temperature. After 20 h, the reaction mixture was diluted with water and ether. The layers were separated and the aqueous layer was extracted with ether. The combined organic extracts were washed with brine solution, dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed through silica gel that was slurry-packed with a 1% triethylamine/pentane solution. Elution with a 1% ether/pentane solution afforded 0.105 g (52%) of the desired bis enol ether. The range of yields obtained for this reaction varied from 20 to 58% over five trials. The spectral data for the mixture of olefin isomers are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 6.20 (dd, J = 12.6 Hz, 1.2 Hz, 0.8 H), 5.96 (dt, J_d = 5.0 Hz, J_t = 1.4 Hz, 0.2 H), 4.81–4.69 (m, 0.7 H), 4.46–4.34 (m, 1.3 H), 3.57, 3.56, 3.524, 3.516, 3.507 (5 s, 6 H), 1.98–1.75 (m, with 2 s at 1.84 and 1.76, 7 H), 0.84, 0.83, 0.82, 0.81 (4 s, 6 H); ^{13}C NMR ($CDCl_3$/75 MHz) 154.7, 152.6, 148.9, 148.7, 147.7, 147.6, 105.5, 104.1, 100.2, 100.0, 99.7, 93.9, 93.6, 59.8, 56.4, 56.3, 55.8, 54.3, 40.10, 40.07, 39.2, 36.6, 35.9, 35.0, 34.1, 27.5, 26.8, 26.7, 17.7, 16.6, 16.5, 14.8; IR (neat/NaCl) 3058, 3040, 2993, 2947, 2835, 1669, 1664, 1466, 1382, 1364, 1346, 1302, 1265, 1251, 1213, 1130, 1110, 1057, 936 cm^{-1}; GCMS (PCI) m/e (rel intensity) peak 1, 198 (M^+, 1), 167 (M^+ − OCH_3, 6), 135 (M^+ − $C_2H_7O_2$, 9), 113 (2), 109 (2), 95 (6), 89 (7), 85 (13), 76 (13), 75 (100), 71 (6), 61 (3), 59 (7); peak 2, 167 (7), 135 (11), 109 (3), 107 (3), 95 (10), 89 (7), 85 (15), 76 (12), 75 (100), 71 (9), 61 (4), 59 (15); HRMS (EI) m/e calcd for $C_{12}H_{22}O_2$ 198.1620, found 198.1622.

4,4-Dimethyl-1-(dimethoxymethyl)-2-(1-oxoethyl)cyclopentane (9). To a three-neck round bottom flask were added 0.280 g (1.4 mmol) of **8**, 35 mL of acetonitrile, 3.6 mL of methanol, 1.0 mL (14 mmol) of 2,6-lutidine, and 1.9 g (28 mmol) of $LiClO_4$. The mixture was stirred in order to dissolve the electrolyte and was then degassed by bubbling nitrogen through the solution. Platinum gauze was used as the anode and a carbon rod was used

(12) The synthesis of **27b** is detailed in the Experimental Section. Substrate **27a** was made in a similar fashion except for the final introduction of the double bonds. For **27b**, 2-(4-hydroxybutyl)cyclohexanone was oxidized to the keto aldehyde and then both enol ethers were introduced at the same time. For **27a** the enol ether was introduced with a Wittig reaction on 2-(4-hydroxybutyl)cyclohexanone followed by Swern oxidation and then introduction of the allylsilane moiety with a second Wittig reaction.

(13) For a description of general data, please see: Wong, P. L.; Moeller, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 11434.

as the cathode. Current was passed at a constant rate of 15 mA until 270 C (2.0 F/mol) had been passed. At this point, the reaction was complete as evidenced by TLC. The reaction was diluted with water and ether and the organic layer was separated. The aqueous layer was extracted with ether. The combined organic extracts were concentrated *in vacuo* and treated with 0.10 g of toluenesulfonic acid in 50 mL of acetone. After 5 h, the reaction was concentrated to a smaller volume and then diluted with ether and water. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic extracts were washed with brine solution, dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed through silica gel using 30% ether/pentane as eluant to afford 0.186 g (62%) of the cyclized products. The spectral data for the mixture of cis and trans isomers are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 4.25 (d, J = 8.9 Hz, 0.2 H), 4.17 (d, J = 6.0 Hz, 0.8 H), 3.30, 3.28 (2 s, 6 H), 2.98–2.82 (m, 1.65 H), 2.76–2.63 (m, 0.35 H), 2.18 (s, 3 H), 1.82–1.70 (m, 0.85 H), 1.68–1.46 (m, 2.3 H), 1.42–1.32 (m, 0.85 H), 1.10, 1.04, 1.02, 0.97 (4 s, 6 H); ^{13}C NMR ($CDCl_3$/75 MHz) 212.2, 211.5, 107.8, 105.6, 53.8, 53.6, 52.7, 51.9, 50.1, 44.7, 44.6, 44.0, 43.5, 42.9, 42.3, 38.8, 38.5, 32.0, 29.4, 28.9, 27.9; IR (neat/NaCl) 2953, 2929, 2866, 2831, 1710, 1465, 1386, 1366, 1181, 1133, 1103, 1061, 976, 959, 909 cm^{-1}; GCMS (PCI) m/e (rel intensity) 169 (40), 167 (8), 152 (18), 151 ($M^+ - C_2H_7O_2$, 100), 150 (12), 140 (11), 125 (8), 110 (10), 109 (84), 75 (13), 61 (9), 59 (11); HRMS (EI) m/e calcd for $C_{12}H_{22}O_3$, 214.1569, found 214.1567.

4,4-Dimethyl-1-(1-oxoethyl)-2-cyclopentanecarboxaldehyde. A solution of 0.110 g (0.5 mmol) of **9** in 2.5 mL of a 1.5% water/acetone mixture was treated with 0.30 g of Amberlyst-15. After 3 h, the reaction was filtered, concentrated *in vacuo*, and chomatographed through silica gel. Elution with 5% ether/pentane afforded 0.080 g (95%) of the deprotected aldehyde products. The spectral data are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 9.73 (s, 1 H), 3.50–3.37 (m, 2 H), 2.20 (s, 3 H), 1.92–1.71 (m, 3 H), 1.64–1.57 (m, 1 H), 1.05, 0.96 (2 s, 6 H); ^{13}C NMR ($CDCl_3$/75 MHz) 208.6, 202.5, 52.4, 51.1, 44.0, 43.9, 39.8, 28.9, 28.5, 27.8; IR (neat/NaCl) 2956, 2868, 2719, 1710, 1384, 1362, 1184, 1089, 895 cm^{-1}; GCMS (PCI) m/e (rel intensity) 169 (M^+ + 1, 17), 168 (M^+, 4), 167 (7), 152 (14), 151 (100), 150 (17), 149 (5), 140 (7), 123 (11), 110 (11), 109 (95), 108 (13), 107 (9); HRMS (EI) m/e calcd for $C_{10}H_{16}O_2$, 168.1150, found 168.1159. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 70.96; H, 9.47.

5,5-Dimethyl-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (10). A 0.020 g (0.12 mmol) solution of 4,4-dimethyl-1-(1-oxoethyl)-2-cyclopentanecarboxaldehyde in 1.5 mL of diethyl ether and 3 mL of THF was treated with 1.5 mL of 5% aqueous KOH and 4 drops of 40% aqueous tetrabutylammonium hydroxide. The reaction mixture was vigorously stirred and refluxed. After 18 h, the reaction was diluted with ether and water. The layers were separated and the aqueous layer was extracted with ether. The combined organic extracts were washed with brine solution, dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed through silica gel. Elution with 2% ether/pentane afforded 0.012 g (67%) of the bicyclic enone. The spectral data are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 7.63 (dd, J = 5.6 Hz, 2.8 Hz, 1 H), 5.98 (dd, J = 5.6 Hz, 1.8 Hz, 1 H), 3.53–3.40 (m, 1 H), 2.95–2.86 (m, 1H), 1.88–1.72 (m, 2 H), 1.50–1.42 (m, 1 H), 1.29–1.20 (m, 1 H), 1.02, 0.99 (2 s, 6 H); ^{13}C NMR ($CDCl_3$/75 MHz) 168.2, 132.2, 50.7, 48.0, 44.4, 44.1, 42.6, 29.1, 28.5; IR (neat/NaCl) 2954, 2930, 2862, 1707, 1581, 1465, 1447, 1386, 1367, 1346, 1308, 1209, 1179, 1085, 805 cm^{-1}; GCMS (PCI) m/e (rel intensity) 151 (M^+ + 1, 100), 150 (27), 149 (8), 135 (10), 123 (8), 95 (5), 94 (5); HRMS (EI) m/e calcd for $C_{10}H_{14}O$ 150.1047, found 150.1043; Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.34. Found: C, 79.71; H, 9.31.

3,3-Dimethyl-6-methyl-7-(trimethylsilyl)-5-(*E,Z*)-hepten-1-ol (15). To a stirred suspension of 62.0 g (167.1 mmol) of ethyltriphenylphosphonium bromide in 350 mL of THF at 0 °C was added 73.5 mL (183.8 mmol) of a 2.5 M n-butyllithium in hexane solution over a 30 min period with the use of an addition funnel. The yellow solution was allowed to warm to room temperature, stirred for 1 h, and then cooled to 0 °C. To this solution was added 24.8 mL (167.2 mmol) of iodomethyltrimethylsilane. The reaction was again allowed to warm to room temperature. After 1 h the reaction was cooled to −78 °C and treated with an additional 73.5 mL (183.8 mmol) of a 2.5 M solution of n-butyllithium in hexane. The resulting dark red solution was allowed to warm to room temperature and then stirred for 1.5 h. The reaction was cooled to −78 °C and a 7.24-g (55.7 mmol) solution of 2-hydroxy-4,4-dimethyltetrahydropyran in 55 mL of THF was cannulated into the stirring ylide solution. The reaction was allowed to warm to room temperature slowly. After 20 h, the reaction was diluted with water and ether. The layers were separated and the aqueous layer was extracted with ether. The combined organic layers were washed with brine solution, dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed through silica gel that was slurry-packed with a 1% triethylamine/hexane solution. Elution with 10% ether/hexane afforded 6.0 g (50%) of the desired alcohol allylsilane. The spectral data for the mixture of olefin isomers are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 5.03 (td, J_t = 8.0 Hz, J_d = 19.0 Hz, 1 H), 3.69 (td, J_t = 7.5 Hz, J_d = 4.0 Hz, 2 H), 1.90 (d, J = 7.6 Hz, 1 H), 1.82 (d, J = 7.1 Hz, 1 H), 1.69 (d, J = 1.2 Hz, 1 H), 1.59 (s, 2 H), 1.53 (t, J = 7.7 Hz, 2 H), 1.50 (s, 2 H), 0.897, 0.890 (2 s, 6 H), 0.021, 0.013 (2 s, 9 H); ^{13}C NMR ($CDCl_3$/75 MHz) 134.6, 134.4, 118.7, 118.1, 59.8, 44.3, 44.2, 40.9, 40.7, 33.4, 33.0, 30.3, 27.4, 27.3, 26.6, 23.3, 18.9, 0.43, −0.58, −1.1; IR (neat/NaCl) 3376 (br), 3020, 2956, 2874, 1653, 1457, 1384, 1365, 1249, 1167, 1112, 1024, 909, 849, 736 cm^{-1}; GCMS (PCI) m/e (rel intensity) peak 1, 229 (M^+ + 1, 2), 228 (M^+, 1), 213 (11), 169 (11), 141 (12), 137 (10), 111 (10), 97 (13), 83 (89), 75 (12), 73 ($^+$SiMe$_3$, 100), 71 (15), 69 (63), 57 (27); peak 2, 229 (2), 228 (1), 213 (10), 141 (11), 137 (9), 111 (9), 97 (12), 83 (87), 75 (15), 74 (9), 73 (100), 71 (14), 69 (63), 57 (27); HRMS (EI) m/e calcd for $C_{13}H_{28}OSi$, 228.1909, found 228.1922. Anal. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35; Si, 12.30. Found: C, 68.61; H, 12.36; Si, 12.14.

1-Methoxy-4,4,7-trimethyl-8-(trimethylsilyl)-1,6-(*E,Z*)-octadiene (16). To a stirred suspension of 11.27 g (32.9 mmol) of (methoxymethyl)triphenylphosphonium chloride in 60 mL of THF at −78 °C was added 19.34 mL (32.9 mmol) of a 1.7 M solution of t-butyllithium in hexane. The resulting dark red solution was allowed to warm to room temperature slowly. In a separate flask, a solution of 2.55 g (11.2 mmol) of **15** and 1.03 mL (14.5 mmol) of dimethyl sulfoxide in 22 mL of THF at −78 °C was treated with 1.17 mL (13.4 mmol) of oxalyl chloride. The reaction was stirred at −78 °C for 30 min and then 4.71 mL (33.5 mmol) of triethylamine was added. After 10 min at −78 °C, the reaction was diluted with 20 mL of THF and was removed from the cold bath. The white ammonium salts were removed by suction filtration and the residue was washed with THF. The combined filtrates were concentrated to a smaller volume and cannulated into the stirring −78 °C ylide solution generated above. The resulting mixture was allowed to warm to room temperature slowly. After 18 h, the reaction was diluted with water and ether. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic extracts were washed with brine solution, dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed through silica gel that was slurry-packed using a 1% triethylamine/hexane solution. Elution with hexane afforded 1.51 g (54%) of the desired olefin. The spectral data for the mixture of olefin isomers are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 6.22 (d, J = 12.4 Hz, 0.6 H), 5.94 (d, J = 6.2 Hz, 0.4 H), 5.05 (m, 1 H), 4.72 (m, 0.6 H), 4.37 (m, 0.4 H), 3.560, 3.556, 3.52, 3.51 (4 s, 3 H), 1.96 (d, J = 7.7 Hz, 1 H), 1.88 (d, J = 7.0 Hz, 0.5 H), 1.81 (d, J = 6.0 Hz, 1 H), 1.79 (d, J = 6.6 Hz, 1 H), 1.69 (d, J = 1.5 Hz, 1H), 1.58 (s, 2 H), 1.50 (s, 2 H), 0.84, 0.82 (2 s, 6 H) 0.02, 0.01 (2 s, 9 H); ^{13}C NMR ($CDCl_3$/75 MHz) 148.2, 148.1, 147.0, 134.1, 134.0, 133.9, 119.5, 119.2, 118.8, 118.6, 103.8, 99.6, 99.5, 59.3, 55.9, 40.3, 40.2, 40.1, 40.0, 39.9, 35.94, 35.88, 34.8, 34.7, 34.3, 34.2, 30.3, 26.6, 23.3, 23.2, 18.9, −0.57, −1.10; IR (neat/NaCl) 3038, 2955, 2903, 1664, 1653, 1466, 1391, 1382, 1364, 1248, 1211, 1134, 1110, 846 cm^{-1}; GCMS (PCI) m/e (rel intensity) 255 (M^+ + 1, 2), 254 (3), 239 (17), 151 (23), 149 (11), 141 (14), 109 (18), 96 (9), 95 (100), 89 (38), 81 (30), 73 (84), 71 (22), 69 (12); HRMS (EI) m/e calcd for $C_{15}H_{30}OSi$, 254.2066, found 254.2058. Anal. Calcd for $C_{15}H_{30}OSi$: C, 70.79; H, 11.88; Si, 11.04. Found: C, 70.80; H, 11.84; Si, 10.42.

4,4-Dimethyl-1-(dimethoxymethyl)-2-(1-methyl-1-ethenyl)-cyclopentane (17). To 0.322 g (1.27 mmol) of **16** in 32 mL of THF and 32 mL of methanol were added 1.75 g (12.7 mmol) of potassium carbonate and 3.4 g (32 mmol) of lithium perchlorate. The resulting mixture was stirred until all of the electrolyte was dissolved in solution and then degassed by sonication for 10 min. The electrodes were inserted into the flask using a two-hole septum equipped with a nitrogen inlet. A reticulated vitreous

carbon anode and a platinum wire cathode were used. The reaction mixture was cooled to 0 °C and current was passed at a constant rate of 20 mA and until 249 C (2.0 F/mol) of electricity had been passed. The reaction mixture was filtered to remove the potassium carbonate, concentrated to a smaller volume, and then worked up with water. The organic layer was separated and the water layer was extracted with ether. The combined ether extracts were washed with brine solution, dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed through silica gel that was slurry-packed with a 1% triethylamine/pentane solution. Elution with pentane afforded 0.240 g (89%) of the cyclized products. The spectral data for the mixture of cis and trans isomers are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 4.80 (d, J = 1.5 Hz, 0.84 H), 4.76 (d, J = 1.8 Hz, 0.16 H), 4.72 (d, J = 1.5 Hz, 0.14 H), 4.70 (s, 0.86 H), 4.17 (d, J = 5.1 Hz, 0.16 H), 4.10 (d, J = 6.8 Hz, 0.84 H), 3.38, 3.31, 3.27 (3 s, 6 H), 2.73 (q, J = 7.8 Hz, 1 H), 2.51 (dt, J_d = 7.4 Hz, J_t = 2 Hz, 1 H), 1.79, 1.72 (2 s, 3 H), 1.67–1.57 (m, 2 H), 1.55–1.42 (m, 2 H), 1.09, 1.03, 1.00 (3 s, 6 H); ^{13}C NMR ($CDCl_3$/75 MHz) 147.3, 146.8, 110.2, 110.0, 108.0, 105.8, 55.1, 54.4, 54.3, 52.3, 49.5, 47.3, 46.7, 45.6, 45.2, 43.8, 41.8, 41.7, 37.1, 37.0, 30.8, 30.4, 30.2, 29.9, 24.0, 19.6; IR (neat/NaCl) 3076, 2951, 2866, 2828, 1646, 1457, 1383, 1366, 1190, 1131, 1062, 937, 910, 885 cm^{-1}; GCMS (PCI) m/e (rel intensity) 181 ($M^+ - OCH_3$, 100), 180 (13), 179 (20), 165 (28), 150 (24), 149 (94), 147 (25), 133 (19), 123 (49), 107 (37), 93 (18), 69 (24); HRMS (EI) m/e calcd for $C_{13}H_{24}O_2$ 212.1776, found 212.1776. Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.99; H, 11.59.

5,5-Dimethyl-4,5,6,6a-tetrahydropentalen-1(3*H*)-one (10 from 17). A solution of 0.37 g (1.74 mmol) of 17 in 70 mL of methanol and 17.5 mL of dichloromethane at −78 °C was treated with ozone generated by silent discharge. The ozone was allowed to bubble through the reaction for an additional 10 min at −78 °C after the reaction turned blue, and then 0.262 g (4.0 mmol) of zinc dust and 0.62 mL (10.8 mmol) of glacial acetic acid were added. The reaction was allowed to warm to room temperature. After 4 h, the reaction was filtered to remove excess zinc dust and concentrated to a smaller volume. The resulting solution was diluted with water and ether. The organic layer was separated and the water layer was extracted with ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed through silica gel that was slurry-packed with a 1% triethylamine/pentane solution. Elution with pentane afforded 0.315 g (84%) of **9**. The NMR data for the mixture of cis and trans isomers are the same as that reported above. This product was treated with 0.10 g of Amberlyst-15 in 10 mL of acetone for 2 h and then filtered and concentrated *in vacuo*. The crude product was then treated with 6 mL of 5% aqueous KOH and 5 drops of 40% aqueous tetra-*n*-butylammonium hydroxide in 6 mL of ether and 12 mL of THF. The resulting mixture was vigorously stirred and refluxed for 15 h. The reaction was then cooled to room temperature and worked up with water and ether. The organic layer was separated and the water layer was extracted with ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed through silica gel. Elution with pentane afforded 0.91 g (62% from **9**) of the desired bicyclic enone **10**. The spectral data are identical to that reported above.

2-(2-Propenyl)cyclohexanone, Dimethyl Acetal. A slurry of 53.4 g (504 mmol) of trimethyl orthoformate and 36 g of K-10 Montmorillonite clay was allowed to stir for 10 min at room temperature. A solution of 16.4 g (119 mmol) of 2-(2-propenyl)-cyclohexanone in 120 mL of pentane was added, and the reaction was stirred for an additional 20 min. The crude reaction mixture was filtered, dried over sodium sulfate, concentrated *in vacuo*, and chromatographed on 200 g of silica that was packed with 10% ether/pentane containing 1% triethylamine. The column was eluted with 10% ether/pentane to afford 20.0 g (91%) of the desired product. The spectral data are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 5.81–5.69 (m, 1 H), 5.04 (d, 1 H, J = 17.1 Hz), 5.00 (d, 1 H, J = 7.9 Hz), 3.17, 3.16 (2 s, 6 H), 2.25–1.74 (m, 4 H), 1.60–1.53 (m, 3 H), 1.43–1.35 (m, 4 H); ^{13}C NMR ($CDCl_3$/75 MHz) 138.0, 115.6, 101.8, 47.2, 46.8, 38.6, 31.2, 27.6, 24.3, 22.2, 19.4; IR (neat/NaCl) 3076, 2960, 2862, 2828, 1640, 1464, 1451, 1370, 1271, 1172, 1048, 911 cm^{-1}; GC/MS (PCI) m/e (rel intensity) 185 (M^+ + 1, 13), 184 (M^+, 4.3), 154 ($M^+ - CH_3O$, 20), 153 (100), 139 (4.7), 112 ($M^+ - C_4H_8O$, 5.7), 111 (34), 97 (2), 73 (10); HRMS (EI) m/e calcd for $C_{11}H_{20}O_2$ 184.1463, found 184.1468.

2-(3-Hydroxypropyl)cyclohexanone, Dimethyl Acetal. To a stirred 0 °C solution of 10.5 mL (105 mmol) of 10 M borane–methyl sulfide in THF in 10.5 mL of additional THF under nitrogen was added 13.7 g (196 mmol) of 2-methyl-2-butene over 10 min. The ice bath was removed and the reaction allowed to stir for 2 h at room temperature. The temperature was decreased to 0 °C and a solution of 11.9 g (64.7 mmol) of 2-(2-propenyl)-cyclohexanone, dimethyl acetal in 120 mL of THF was added dropwise over 30 min. After an additional 1.5 h of stirring at 0 °C, the reaction was treated dropwise with a solution of 11.8 g (300 mmol) of H_2O_2 in 65 mL of 3 N NaOH. The reaction was allowed to stir for 16 h at room temperature, diluted with ether, washed with saturated sodium sulfite, and washed with aqueous K_2CO_3. The aqueous fractions were combined and extracted with ether. The organic fractions were combined, washed with brine (100 mL), dried over K_2CO_3, and concentrated *in vacuo*. The crude reaction mixture was chromatographed through silica gel with 40% ether/pentane as the eluant to afford 13.1 g (100%) of the desired alcohol. The spectral data are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 3.67 (t, 2 H, J = 6.0 Hz), 3.17, 3.15 (2 s, 6 H), 1.85–1.33 (m, 14 H); ^{13}C NMR ($CDCl_3$/75 MHz) 102.2, 62.9, 47.2, 46.9, 38.7, 31.0, 27.6, 24.7, 22.4, 22.2, 19.5; IR (neat/NaCl) 3445, 3348, 2962, 2828, 1457, 1365, 1271, 1168, 1082, 1049, 1017, 947, 870 cm^{-1}; GC/MS (PCI) m/e (rel intensity) 201 ($M^+ - 1$, 0.2), 171 ($M^+ - CH_3O$, 14), 169 (11), 139 ($M^+ - C_2H_7O_2$, 100), 121 (21), 111 (42), 81 (5.2); HRMS (EI) m/e calcd for $C_{11}H_{22}O_3$ 202.1568, found 202.1563.

2-(3-(*tert*-Butyldiphenylsiloxy)propyl)cyclohexanone. A solution of 11.4 g (57 mmol) of 2-(3-hydroxypropyl)cyclohexanone, dimethyl acetal, 17.1 g (62 mmol) of *tert*-butylchlorodiphenylsilane, and 8.3 g (124 mmol) imidazole in 100 mL of DMF under nitrogen was allowed to stir overnight at room temperature. The reaction was diluted with ether and then washed with water and brine. The aqueous fractions were combined and extracted with ether. The organic fractions were combined, dried over Na_2SO_4, concentrated *in vacuo*, and chromatographed through silica gel with 25% ether/pentane as the eluant. Due to partial deprotection of the ketone this material was not characterized but carried on to the next step. A solution of this protected alcohol in 500 mL of THF at 0 °C was treated with 250 mL of 0.5 N hydrochloric acid. The reaction was allowed to stir for 30 min at room temperature, after which the THF was taken off *in vacuo* and the aqueous layer extracted with ether. The combined organic fractions were washed with brine, dried over Na_2SO_4, concentrated *in vacuo*, and chromatographed through silica gel with 10% ether/pentane as the eluant to afford 21 g (95% over two steps) of the desired product. The spectral data are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 7.69–7.66 (m, 4H), 7.42–7.38 (m, 6H), 3.65 (t, 2H, J = 6.4 Hz), 2.40–1.20 (m, 13 H), 1.07, 1.05 (2 s, 9H); ^{13}C NMR ($CDCl_3$/75 MHz) 213.8, 135.7, 135.0, 134.1, 129.6, 127.7, 63.8, 50.2, 41.8, 33.7, 29.8, 27.8, 26.6, 26.3, 25.5, 24.6, 18.9; IR (neat/NaCl) 3070, 3050, 2928, 2856, 1710, 1473, 1428, 1111, 822 cm^{-1}; GC/MS (PCI) m/e (rel intensity) 395 (M^+ + 1, 1.0), 394 (M^+, 1.1), 379 ($M^+ - CH_3$, 0.7), 337 ($M^+ - C_4H_9$, 2.7), 317 ($M^+ - C_6H_5$, 7.1), 199 (2.6), 179 (4.1), 139 ($M^+ - C_{16}H_{19}OSi$, 100), 121 (5.6), 79 (20); HRMS (EI) m/e calcd for $C_{21}H_{25}O_2Si$ ($M^+ - C_4H_9$) 337.1623, found 337.1625.

(*E* and *Z*)-2-(3-(*tert*-Butyldiphenylsiloxy)propyl)-1-(methoxymethylidene)cyclohexane. To a 0 °C solution of 48 g (141 mmol) of (methoxymethyl)triphenylphosphonium chloride in 200 mL of THF was added 56 mL (140 mmol) of a 2.5 M *n*-butyllithium in hexane solution. The resulting red solution was warmed to room temperature and stirred for 1 h. The reaction temperature was decreased to 0 °C and 20.7 g (52.5 mmol) of 2-(3-(*tert*-butyldiphenylsiloxy)propyl)cyclohexanone in 100 mL of THF was added over 20 min. The reaction was warmed to room temperature and stirred 16 h. The reaction was concentrated *in vacuo*, diluted with ether, washed two times with 40% sodium bisulfite, and washed with brine. The aqueous fractions were combined and extracted twice with ether. The organic fractions were combined, dried over K_2CO_3, concentrated *in vacuo*, diluted with pentane to precipitate the triphenylphosphine oxide, filtered, and concentrated *in vacuo*. The crude reaction was chromatographed through silica gel with a gradient elution from 100% hexane to 5% ether/hexane as eluant to afford 10.0

g (44%) of the pure product. In addition, 14.2 g of product contaminated with triphenylphosphine oxide was obtained. Integration of the 300-MHz ^{1}H NMR obtained for this sample indicated that it contained an additional 7.5 g (32%) of the desired product. Spectral data are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 7.69–7.66 (m, 4 H), 7.42–7.35 (m, 6 H), 5.75 (d, 0.36 H, J = 1.8 Hz), 5.68 (s, 0.64 H), 3.66 (app q, 2 H, J = 6.1 Hz), 3.51, 3.44 (2 s, 3 H), 2.83–2.75 (br m, 0.36 H), 2.14–1.30 (m, 12.64 H), 1.05, 1.04 (2 s, 9 H); ^{13}C NMR ($CDCl_3$/75 MHz) 139.8, 139.2, 135.8, 134.4, 134.3, 129.7, 129.6, 127.7, 121.1, 120.6, 64.1, 59.2, 59.0, 38.7, 33.5, 32.3, 31.2, 30.4, 28.3, 27.7, 27.2, 27.1, 26.7, 26.3, 23.3, 22.9, 21.3, 19.0; IR (neat/NaCl) 3070, 2928, 2857, 1680, 1473, 1428, 1231, 1201, 1111, 823 cm^{-1}; GC/MS (PCI) m/e (rel intensity) peak 1 423 ($M^+ - CH_3$, 7.0), 407 ($M^+ - CH_3O$, 3.7), 391 ($M^+ - C_2H_7O$, 8.2), 365 (24), 346 ($M^+ - C_7H_8$, 12), 345 (40), 167 (37), 165 (15), 135 (100), 109 (15), 79 (26), peak 2 423 ($M^+ - CH_3$, 3.2), 407 ($M^+ - CH_3O$, 1.4), 391 ($M^+ - C_2H_7O$, 4.0), 365 (11), 346 ($M^+ - C_7H_8$, 5.0), 345 (18), 167 (30), 165 (15), 135 (100), 109 (16), 79 (20).

(*E* and *Z*)-2-(3-Hydroxypropyl)-1-(methoxymethylidene)-cyclohexane (19). A solution of 10.0 g (23 mmol) of (*E* and *Z*)-2-(3-(*tert*-butyldiphenylsiloxy)propyl)-1-(methoxymethylidene)-cyclohexane in 45 mL (45 mmol) 1 M tetrabutylammonium fluoride was allowed to stir for 4 h at room temperature. The reaction was diluted with ether and then washed with water and brine. The organic fractions were combined, saturated with sodium chloride, and extracted with ether. All organic fractions were combined, dried over potassium carbonate, and concentrated *in vacuo*. The crude product was chromatographed through 200 g of silica gel packed with a 40% ether/pentane solution containing 1% triethylamine. The column was eluted with 40% ether/hexane to afford 4.0 g (96%) of the desired product. The spectral data are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 5.80 (d, 0.33 H, J = 2.0 Hz), 5.74 (s, 0.67 H), 3.65 (br s, 2 H), 3.54, 3.51 (2 s, 3 H), 2.87–2.83 (m, 0.33 H), 2.27–1.31 (m, 13.67 H); ^{13}C NMR ($CDCl_3$/75 MHz) 139.8, 139.2, 120.8, 120.3, 62.9, 59.2, 59.0, 38.7, 33.3, 32.2, 31.2, 30.7, 30.4, 28.1, 27.6, 27.3, 27.1, 26.2, 23.0, 22.7, 21.2; IR (neat/ NaCl) 3430, 3295, 2951, 2850, 1679, 1447, 1378, 1231, 1201, 1059, 911 cm^{-1}; GC/MS (PCI) m/e (rel intensity) 185 ($M^+ + 1$, 5.4), 184 (M^+, 12), 183 ($M^+ - 1$, 17), 167 ($M^+ - OH$, 9.1), 153 ($M^+ - CH_3O$, 27), 136 ($M^+ - CH_4O_2$, 21), 125 (16), 109 (14), 93 (2.3), 71 (2.8); HRMS (EI) m/e calcd for $C_{11}H_{22}O_2$ 184.1463, found 184.1449.

1-(Methoxy-(*E,Z*)-methylidene)-2-(4-methyl-5-(trimethylsilyl)-(*E,Z*)-3-pentenyl)cyclohexane (20). To a stirred suspension of 2.23 g (6.0 mmol) of ethyltriphenylphosphonium bromide in 10 mL of THF at 0 °C was added 2.66 mL (6.7 mmol) of a 2.5 M *n*-butyllithium in hexane solution. This mixture was warmed to room temperature, allowed to stir for 1 h, and then cooled to 0 °C. To this mixture was added 0.89 mL (6.0 mmol) of (iodomethyl)trimethylsilane. The mixture was allowed to warm to room temperature. After 1 h, the reaction was cooled to −78 °C and treated with an additional 2.66 mL (6.7 mmol) of a 2.5 M *n*-butyllithium in hexane solution. The resulting dark red solution was allowed to warm to room temperature and then stirred for 1.5 h. In a separate flask, 0.368 g (2.0 mmol) of 2-(3-hydroxypropyl)-1-(methoxy-(*E,Z*)-methylidene)cyclohexane and 0.184 mL (2.6 mmol) of dimethyl sulfoxide at −78 °C in 4 mL of THF were treated with 0.209 mL (2.4 mmol) of oxalyl chloride. The resulting mixture was stirred for 20 min at −78 °C, and then the reaction was quenched with 0.84 mL (6.0 mmol) of triethylamine. After 10 min, the reaction was diluted with 10 mL of THF and allowed to warm to room temperature. The white solids were removed by suction filtration and washed with THF. The volume of the combined filtrates was reduced *in vacuo* and then cannulated into the ylide solution formed above at −78 °C. The reaction was allowed to slowly warm to room temperature and stirred for 18 h. The reaction was diluted with ether and water, the organic layer was separated, and the aqueous layer was extracted with ether. The combined organic extracts were washed with brine solution, dried over $MgSO_4$, concentrated *in vacuo*, and then chromatographed through silica gel that was slurry-packed with a 1% triethylamine/hexane solution. Elution with hexane afforded 1.82 g (53%) of the desired olefin. The spectral data for the mixture of olefin isomers are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 5.75 (s, 0.36 H), 5.69 (s, 0.64 H), 5.05–4.87 (m, 1 H), 3.52, 3.48 (2 s, 3 H), 2.85–2.25 (m, 1 H), 2.20–1.15 (m with 2 s at 1.64 and 1.56, 17 H), −0.002, −0.024 (2 s, 9 H); ^{13}C NMR ($CDCl_3$/75 MHz) 140.83, 140.76, 140.3, 140.2, 134.1, 133.7, 133.6, 133.3, 124.3, 124.0, 123.6, 122.3, 122.2, 121.9, 121.7, 67.1, 60.6, 60.41, 60.37, 40.0, 39.7, 34.82, 34.75, 34.2, 34.0, 33.4, 33.3, 33.1, 33.0, 32.6, 32.5, 31.1, 31.0, 29.82, 29.76, 28.7, 28.6, 28.1, 27.9, 27.6, 27.5, 27.4, 24.7, 24.5, 24.3, 22.90, 22.86, 19.9, 19.8, 16.5, 1.24, 0.56, −0.05; IR (neat/NaCl) 2928, 2854, 2680, 1457, 1447, 1248, 1234, 1202, 1128, 857, 841 cm^{-1}; GCMS (PCI) m/e (rel intensity) 281 ($M^+ + 1$, 2), 280 (2), 265 ($M^+ - CH_3$, 11), 177 (6), 175 (11), 145 (20), 126 (12), 122 (20), 116 (6), 95 (6), 89 (11), 81 (12), 74 (8), 73 ($^+SiMe_3$, 100); HRMS (EI) m/e calcd for $C_{17}H_{32}OSi$ 280.2222, found 280.2226. Anal. Calcd for $C_{17}H_{32}OSi$: C, 72.78; H, 11.50. Found: C, 72.52; H, 11.58.

1-(Methoxy-(*E,Z*)-methylidene)-2-(5-(trimethylsilyl)-(*E,Z*)-3-pentenyl)cyclohexane (21). To a stirred suspension of 13.9 g (39 mmol) of methyltriphenylphosphonium bromide in 80 mL of THF at 0 °C was added 17.2 mL (43 mmol) of a 2.5 M solution of *n*-butyllithium in hexane solution. The mixture was warmed to room temperature, allowed to stir for 1 h, and then cooled to 0 °C. To this mixture was added 5.79 mL (39 mmol) of (iodomethyl)trimethylsilane. The mixture was again allowed to warm to room temperature. After 1 h, the reaction was cooled to −78 °C and treated with an additional 17.2 mL (42 mmol) of a 2.5 M *n*-butyllithium in hexane solution. The resulting dark red solution was allowed to warm to room temperature and then stirred for 3 h. In a separate flask, 2.4 g (13 mmol) of 2-(3-hydroxypropyl)-1-(methoxy-(*E,Z*)-methylidene)cyclohexane and 1.2 mL (17 mmol) of DMSO in 26 mL of THF at −78 °C was treated with 1.36 mL (16 mmol) of oxalyl chloride. The resulting mixture was stirred for 20 min at −78 °C, and then the reaction was quenched with 5.47 mL (39 mmol) of triethylamine. After 15 min, the cold bath was removed and the reaction allowed to warm to room temperature. The salts were removed from the crude reaction by vacuum filtration, and the salts were washed with THF. The crude aldehyde was added to the ylide solution formed above at −78 °C. After 1 h at −78 °C, the cold bath was removed and the reaction allowed to stir for 20 h at room temperature. The reaction was diluted with ether and then washed with saturated sodium sulfite and brine. The organic fractions were combined, dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed through silica gel that was slurry-packed with a 1% triethylamine/hexane solution. The product was eluted with 100% hexane to afford 1.82 g (52% over two steps) of the desired product. The spectral data are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 5.77 (d, 0.55 H, J = 1.8 Hz), 5.70 (s, 0.45 H), 5.41–5.19 (m, 2H), 3.52, 3.48 (2 s, 3H), 2.83–2.78 (br m, 0.55 H), 2.26–1.13 (m, 14.45 H), −0.03, −0.04, −0.044 (3 s, 9 H); ^{13}C NMR ($CDCl_3$/75 MHz) 141.3, 140.8, 129.7, 129.3, 126.9, 126.5, 122.5, 122.1, 60.7, 60.5, 40.0, 34.8, 34.7, 34.2, 33.6, 33.2, 32.8, 32.6, 32.1, 29.8, 28.7, 27.9, 26.6, 26.4, 24.7, 24.3, 23.8, 22.9, 19.7, 19.6, −0.61, −0.82; IR (neat/NaCl) 3005, 2929, 2854, 1680, 1457, 1447, 1248, 1231, 1203, 1129, 855 cm^{-1}; GC/MS (PCI) m/e (rel intensity) 267 ($M^+ + 1$, 42), 266 (M^+, 15), 251 ($M^+ - CH_3$, 100), 235 ($M^+ - CH_3O$, 8.3), 163 (31), 144 (36), 125 ($M^+ - C_8H_{17}Si$, 35), 73 (82); HRMS (EI) m/e calcd for $C_{16}H_{30}OSi$ 266.2066, found 266.2060. Anal. Calcd for $C_{16}H_{30}OSi$: C, 72.11; H, 11.35. Found: C, 71.56; H, 11.31.

7a-(Dimethoxymethyl)-1-(1-methyl-1-ethenyl)octahydro-1*H*-indene (22). A 0.487-g (1.7 mmol) solution of **20** in 15 mL of THF was cannulated into a 100-mL round bottom flask containing 40 mL of methanol, 4.26 g of $LiClO_4$ (40 mmol), and 2.3 g (17 mmol) of potassium carbonate. An additional 25 mL of THF was added and the reaction was stirred and then degassed by sonicating the solution for 10 min. Reticulated vitreous carbon was used as the anode and a carbon rod was used as the cathode. The reaction mixture was cooled to 0 °C and current was passed at a constant rate of 25 mA until 2.1 F/mol of electricity had been passed. Most of the THF was removed and then the reaction was diluted with ether and water. The organic layer was separated and the water layer extracted with ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed through silica gel that was slurry-packed with a 1% triethylamine/hexane solution. Elution with hexane afforded 0.25 g (62%) of the cyclized product along with 0.033 g (7%) of the recovered starting material. The spectral data for the mixture of cis and trans isomers are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 4.77, 4.70 (2 s, 2 H), 4.27, 3.90 (2 s, 1 H), 3.53, 3.48, 3.46, 3.38 (4 s, 6 H), 2.70 (t, J = 9 Hz, 0.33 H), 2.58

(t, J = 8 Hz, 0.67 H), 2.18–2.04 (m, 1 H), 1.89–1.20 (broad m with a singlet at 1.77, 15 H); ^{13}C NMR ($CDCl_3$/75 MHz) 147.4, 146.8, 111.9, 111.2, 111.1, 110.8, 59.5, 59.0, 57.9, 57.8, 52.9, 50.4, 50.3, 50.1, 40.0, 39.3, 29.1, 28.8, 28.3, 27.2, 26.8, 26.0, 25.96, 25.10, 24.5, 23.8, 23.1, 21.9, 21.3, 20.4; IR (neat/NaCl) 3100, 2931, 2865, 2828, 1637, 1448, 1370, 1187, 1119, 1071, 992, 969, 914, 884, 733 cm^{-1}; GCMS (PCI) m/e (rel intensity) 207 ($M^+ - CH_3O$, 2), 206 ($M^+ - CH_3OH$, 2), 193 (57), 175 (92), 173 (27), 149 (27), 147 (38), 133 (38), 109 (71), 95 (51), 83 (61), 73 (74), 71 (100), 69 (40); HRMS (EI) m/e calcd for $C_{15}H_{26}O_2$ 238.1933, found 238.1927.

Octahydro-3*H*-cyclopent[*c*]inden-3-one (23). A solution of 0.12 g (0.50 mmol) of 7a-(dimethoxymethyl)-1-(1-methyl-1-ethenyl)octahydro-1*H*-indene in 20 mL of methanol and 5 mL of dichloromethane at −78 °C was treated with ozone. Following the appearance of a blue coloration, ozone was bubbled through the reaction for an additional 10 min. The excess ozone was removed by passing nitrogen though the solution at −78 °C. Nitrogen was passed through the solution for an additional 10 min after the blue coloration disappeared. The reaction was then treated with 0.76 g (1.2 mmol) of zinc dust and 0.18 mL (3.1 mmol) of glacial acetic acid. The reaction was allowed to slowly warm to room temperature. After 5 h, the reaction was concentrated to a smaller volume, the solids were removed by filtration, and the resulting filtrate was diluted with ether and water. The layers were separated, and the aqueous layer was extracted with ether. The combined organic extracts were washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, concentrated *in vacuo*, and treated with 0.30 g of Amberlyst-15 in 3 mL of acetone. After 2 h, the deprotection of the acetals was complete as evidenced by capillary column gas chomatography. The reaction mixture was filtered, concentrated *in vacuo*, and treated with 6 mL of 5% of aqueous KOH and 5 drops of tetra-*n*-butylammonium hydroxide in 6 mL of ether and 12 mL of THF. The reaction was vigorously stirred, refluxed for 8 h, cooled to room temperature, and then diluted with ether and water. The layers were separated, and the water layer was extracted with ether. The combined organic layers were washed with brine solution, dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed through silica gel using gradient elution from pentane to 1% ether/pentane in order to afford 0.060 g (68%) of the desired tricyclic enone. The spectral data are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 7.37 (d, J = 5.4 Hz, 1 H), 6.04 (d, J = 5.7 Hz, 1 H), 2.43 (dd, J = 11.7 Hz, 2.1 Hz, 1 H), 2.25–2.13 (m, 1 H), 1.84–1.47 (m, 8 H), 1.45–1.33 (m, 1 H), 1.32–1.09 (m, 3 H); ^{13}C NMR ($CDCl_3$/75 MHz) 213.8, 173.1, 131.8, 57.2, 53.9, 40.5, 32.8, 30.6, 27.9, 27.6, 24.4, 23.5; IR (neat/NaCl) 3074, 3032, 2934, 2857, 1712, 1586, 1450, 1350, 1342, 1203, 1165, 1115, 911, 798, 732 cm^{-1}; GCMS (PCI) m/e (rel intensity) 177 (M^+ + 1, 100), 176 (17), 175 (9), 159 (4), 149 (3), 135 (3), 121 (2), 81 (2); HRMS (EI) m/e calcd for $C_{12}H_{16}O$ 176.1201, found 176.1213. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.30; H, 9.28.

7a-(Dimethoxymethyl)-1-vinyloctahydro-1*H*-indene (24) and 7a-formyl-1-vinyloctahydro-1*H*-indene. A solution of 4.79 g of lithium perchlorate in 90 mL of 50% methanol/THF containing 0.50 g (1.88 mmol) of enol ether **21** and 2.6 g (18.8 mmol) of potassium carbonate was placed in a three-neck round bottom flask equipped with a reticulated vitreous carbon anode, a platinum wire cathode, and a nitrogen inlet. The reaction was degassed *via* sonication for 5 min, cooled to 0 °C, and electrolyzed at a constant current of 30 mA until 380 C (2.1 F/mol) of charge had been passed. When complete, the reaction was concentrated to a smaller volume and then diluted with water and ether. The organic layer was separated and the aqueous layer extracted with ether. The organic fractions were combined, washed with brine, dried over $MgSO_4$, and chromatographed through silica gel. A gradient elution from 100% hexane to 2% ether/hexane afforded 0.293 g (70%) of the cyclized product. Due to rapid hydrolysis of the dimethoxy acetal, the cyclized product was typically characterized as the aldehyde. The spectral data for the aldehyde as a mixture of cis and trans isomers are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 9.46, 9.33 (2 s, 1 H), 5.76–5.51 (m, 1 H), 4.99–4.88 (m, 2 H), 2.65–2.60 (m, 1H), 2.43–2.37 (br m, 0.5 H), 2.27 (p, 0.5 H, J = 6.8 Hz), 2.06–1.07 (m, 12 H); ^{13}C NMR ($CDCl_3$/75 MHz) 207.3, 206.5, 138.7, 136.7, 116.3, 115.7, 59.1, 58.8, 50.7, 49.9, 40.6, 38.1, 28.8, 28.1, 28.0, 27.1, 26.6, 25.9, 25.4, 22.3, 22.1, 21.6, 19.5; IR (neat/NaCl) 3078, 2930, 2861, 2703, 1721, 1637, 1473, 1447, 996, 915 cm^{-1}; GC/MS (PCI) m/e (rel intensity) 179 (M^+ + 1, 19), 178 (M^+, 6.0), 161 (54), 151 ($M^+ - C_2H_3$, 19), 149 (M^+ − CHO, 28), 122 ($M^+ - C_3H_4O$, 6.7), 109 (24), 95 (100); HRMS (EI) calcd for $C_{12}H_{18}O$ 178.1358, found 178.1346.

7a-Formyl-1-vinyloctahydro-1*H*-indene. The most convenient preparative procedure for cleaving acetal **24** generated from the previous reaction involved treatment of the acetal with Amberlyst-15 in a 1.5% water/acetone mixture as described above for the formation of 4,4-dimethyl-1-(1-oxoethyl)-2-cyclopentanecarboxaldehyde. In this fashion, a 90% isolated yield of the aldehyde could be obtained from **24**. The spectral data are identical to those reported for the preceding experiment.

7a-(1-Hydroxyethyl)-1-vinyloctahydro-1*H*-indene (25). To a 0.390-g (2.2 mmol) solution of 7a-formyl-1-vinyloctahydro-1*H*-indene in 2.5 mL of THF was added 1.09 mL (3.3 mmol) of a 3 M methylmagnesium bromide solution in THF. The reaction was allowed to stir for 3 h and then treated with 2 mL of water. After an additional hour, the reaction was diluted with a saturated NH_4Cl solution and ether. The layers were separated, and the aqueous layer was extracted with ether. The combined organic extracts were washed with brine solution, dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed through silica gel. Elution with 20% ether/hexane afforded 0.408 g (96%) of the desired alcohol. The spectral data of the mixture of isomers are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 6.08 (ddd, J = 17.2 Hz, 9.7 Hz, 8.2 Hz, 0.7 H), 5.95 (m, 0.3 H), 4.11, 4.08, 3.95, 3.94 (4 q, J = 6.4 Hz, 2 H), 2.72 (m, 1 H), 2.04–1.84 (m, 2 H), 1.83–1.12 (m with 2 d at 1.25 and 1.16, J = 7.1 Hz, 15 H); ^{13}C NMR ($CDCl_3$/75 MHz) 142.0, 141.3, 141.1, 115.3, 115.1, 114.3, 71.4, 69.6, 69.5, 52.1, 51.0, 49.7, 48.8, 47.8, 46.8, 40.8, 40.5, 39.3, 29.3, 29.1, 29.0, 28.2, 28.1, 27.9, 26.8, 26.7, 25.9, 24.3, 24.1, 23.9, 23.4, 22.7, 21.3, 21.1, 21.0, 20.1, 19.1, 17.7, 17.6; IR (neat/NaCl) 3409 (br), 3073, 2930, 2872, 1636, 1449, 1376, 1247, 1097, 1053, 1000, 907, 859 cm^{-1}; GCMS (PCI) m/e (rel intensity) 195 (M^+ + 1, 2), 194 (2), 193 (8), 178 (15), 177 (M^+ − OH, 100), 176 (6), 175 (16), 151 (17), 149 (33), 135 (26), 121 (35), 109 (16), 95 (74), 81 (46), 67 (7); HRMS (EI) m/e calcd for $C_{13}H_{22}O$ 194.1671, found 194.1660. Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.22; H, 11.18.

Octahydrocyclopent[*c*]inden-1-one (26). To a solution of 0.284 g (1.5 mmol) of **25** and 0.14 mL (1.9 mmol) of dimethyl sulfoxide in 3 mL of THF at −78 °C was added 0.153 mL (1.8 mmol) of oxalyl chloride. The reaction was allowed to stir at −78 °C for 20 min, after which 0.62 mL (4.4 mmol) of triethylamine was added. After 10 min, the reaction was diluted with 10 mL of THF and allowed to warm to room temperature. The white solids were removed by vacuum filtration, and the residue was washed with THF. The combined filtrates were concentrated *in vacuo*. The crude product was taken up in a mixture of 40 mL of methanol and 10 mL of dichloromethane, the solution was cooled to −78 °C, and ozone was bubbled through until the solution became blue. After the solution turned blue, ozone was bubbled through the reaction for an additional 10 min. The excess ozone was removed by bubbling nitrogen through the solution. This process was continued for 10 min after the disappearance of the blue color. The resulting solution was then treated with 0.22 g (3.37 mmol) of zinc dust and 0.50 mL (9.0 mmol) of glacial acetic acid, and the reaction was allowed to warm to room temperature. After 5 h, the reaction volume was reduced under vacuum and then the reaction filtered to remove the excess zinc. The resulting filtrate was diluted with water and ether, the layers were separated, and the aqueous layer was extracted with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution, dried over $MgSO_4$, and concentrated *in vacuo*. The crude material was treated with 0.10 g of Amberlyst-15 in 7.5 mL of acetone without purification. After 1.5 h, the reaction was filtered and concentrated *in vacuo*. The subsequent product was treated with 6 mL of 5% aqueous KOH and 4 drops of 40% aqueous tetra-*n*-butylammonium hydroxide in 6 mL of ether and 12 mL of THF. The reaction was vigorously stirred, refluxed for 20 h, cooled to room temperature, and then diluted with water and ether. The layers were separated, and the aqueous layer was extracted with ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed through silica gel. Elution with pentane afforded 0.180 g (70% for the four-step sequence) of the tricyclic enone. The spectral data are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 7.58 (dd, J = 5.6 Hz, 3.2 Hz, 1 H), 6.08 (dd, J = 5.6 Hz, 1.2 Hz, 1 H), 2.99 (m, 1 H), 2.20–1.98 (m, 2 H), 1.76–1.07 (m, 11

H); ^{13}C NMR ($CDCl_3$/75 MHz) 216.2, 166.5, 131.5, 59.1, 50.6, 39.7, 31.1, 29.4, 27.7, 26.8, 24.4, 22.9; IR (neat/NaCl) 3074, 3042, 2926, 2854, 1701, 1586, 1451, 1347, 1182, 1033, 826, 798 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 177 (M^+ + 1, 100), 176 (27), 175 (37), 159 (3), 149 (9), 135 (7), 121 (9), 81 (4); HRMS (EI) *m/e* calcd for $C_{12}H_{16}O$ 176.1201, found 176.1199. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.31; H, 9.39.

1,1-Dimethoxy-2-(4-acetoxybutyl)cyclohexane. To a suspension of 7 g of K-10 Montmorillonite clay in 12 mL of trimethyl orthoformate was cannulated a solution of 3.6 g (14.9 mmol) of 2-(4-acetoxybutyl)cyclohexanone[14] in 22 mL of hexane. The reaction was stirred for 1 h and then the clay removed by vacuum filtration. The residue was washed with ether, and the combined filtrates were washed with a saturated $NaHCO_3$ solution, dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed through silica gel that was slurry-packed with a 1% triethylamine/hexane solution. Elution with 20% ether/hexane afforded 3.8 g (99%) of the methoxylated ketone. The spectral data are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 4.07 (t, J = 6.7 Hz, 2 H), 3.16, 3.13 (2 s, 6 H), 2.05 (s, 3 H), 1.82–1.50 (m, 7 H), 1.49–1.19 (m, 8 H); ^{13}C NMR ($CDCl_3$/75 MHz) 172.8, 103.6, 66.1, 48.9, 48.5, 40.7, 30.5, 29.4, 27.7, 26.3, 26.0, 24.0, 22.6, 21.4; IR (neat/NaCl) 2940, 2864, 2829, 1743, 1457, 1449, 1387, 1366, 1241, 1106, 1059, 943, 870 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 227 ($M^+ - OCH_3$, 13), 167 (28), 154 (14), 153 (67), 136 (20), 135 (91), 125 (20), 111 (24), 95 (14), 81 (19), 67 (19), 61 (100); HRMS (EI) *m/e* calcd for $C_{14}H_{26}O_2$, 258.1831, found 258.1830. Anal. Calcd for $C_{14}H_{26}O_2$: C, 65.08; H, 10.14. Found: C, 65.19; H, 9.71.

2-(4-Hydroxybutyl)cyclohexanone. To a 0 °C stirred suspension of 0.46 g (12 mmol) of $LiAlH_4$ in 12 mL of anhydrous ether was cannulated a 1.05-g (4.0 mmol) solution of 1,1-dimethoxy-2-(4-acetoxybutyl)cyclohexane in 12 mL of anhydrous ether for a period of 10 min. The reaction was kept at 0 °C for 1 h and was then allowed to slowly warm to room temperature. After another hour, the reaction was cooled to 0 °C and then quenched by the dropwise addition of 50 mL of methanol followed by the addition of 100 mL of 30% Rochelle's salt solution. The reaction was allowed to warm to room temperature. The organic layer was separated and the aqueous layer was extracted with ether until TLC analysis indicated that no product remained in the aqueous layer. The combined organic extracts were dried with brine solution followed by $MgSO_4$ and then concentrated *in vacuo*. The crude product was treated with 0.24 g of Amberlyst-15 in 20 mL of a 1.5% H_2O/acetone solution at room temperature. After 3 h, the reaction was filtered, concentrated *in vacuo*, and chromatographed through 30 g of silica gel using 25% ether/hexane to afford 0.63 g (3.68 mmol) of the desired product. The spectral data are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 3.60 (t, J = 6.4 Hz, 2 H), 2.44–2.23 (m, 3 H), 2.18–1.98 (m, 2 H), 1.90–1.52 (m, 7 H), 1.47–1.14 (m, 4 H); ^{13}C NMR ($CDCl_3$/75 MHz) 214.2, 62.4, 50.6, 41.9, 33.7, 32.4, 28.7, 27.8, 24.7, 23.0; IR (neat/NaCl) 3400, 2930, 2861, 1708, 1448, 1431, 1311, 1130, 1061, 1042 cm^{-1}; GCMS (PCI) *m/e* (relative intensity): 171 (M^+ + 1, 45), 170 (M^+, 2), 154 (33), 153 (M^+ – OH, 100), 152 (12), 151 (12), 135 (44), 111 (5), 98 (18), 97 (7), 71 (9), 69 (6); HRMS (EI) *m/e* calcd for $C_{10}H_{18}O_2$ 170.1307, found 170.1306. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 72.10; H, 10.82.

1-(Methoxy-(*E,Z*)-methylidene)-2-(5-methoxy-4-(*E,Z*)-pentenyl)cyclohexane (27b). To a stirred suspension of 10.28 g (30.0 mmol) of (methoxymethyl)triphenylphosphonium chloride in 50 mL of THF at 0 °C was added 17.65 mL (30.0 mmol) of a 1.7 M solution of *tert*-butyllithium in hexane solution. The dark red mixture was allowed to stir for 30 min at 0 °C and then allowed to warm to room temperature. In a separate flask, a solution of 0.855 g (5.0 mmol) of 2-(hydroxybutyl)cyclohexanone and 0.60 mL (8.5 mmol) of dimethyl sulfoxide in 15 mL of dichloromethane at –78 °C was treated with 0.62 mL (7.5 mmol) of oxalyl chloride. The reaction was allowed to stir at –78 °C for 30 min and then 2.09 mL of triethylamine added. After 10 min, the reaction was allowed to warm to room temperature, the white solids were removed by vacuum filtration, and the resulting filtrate was concentrated *in vacuo*. The crude product was diluted with 10 mL of THF and cannulated into the stirring 0 °C ylide solution prepared above. The reaction was allowed to warm to room temperature and was stirred overnight. After 18 h, the reaction was diluted with water and ether. The layers were separated, and the aqueous layer was extracted with ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed through silica gel that was slurry-packed using a 1% triethylamine/pentane solution. The column was eluted with pentane to afford 0.652 g (58%) of the desired bis enol ether. The spectral data for the mixture of olefin isomers are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 6.28 (d, J = 13 Hz, 0.7 H), 5.86 (dt, J_d = 6.3 Hz, J_t = 1.5 Hz, 0.3 H), 5.77 (t, J = 2.0 Hz, 0.7 H), 5.72 (br s, 0.3 H), 4.73 (dt, J_d = 12.6 Hz, J_t = 7.3 Hz, 0.7 H), 4.34 (q, J = 7.4 Hz, 0.3 H), 3.58, 3.57, 3.54, 3.53, 3.50, 3.49 (6 s, 6 H), 2.87–2.76 (m, 1 H), 2.33–2.0 (m, 1 H), 2.0–1.84 (m, 2 H), 1.84–1.66 (m, 2 H), 1.64–1.45 (m, 4 H), 1.32–1.10 (m, 5 H); ^{13}C NMR ($CDCl_3$/75 MHz) 148.6, 148.5, 147.7, 147.5, 141.2, 141.1, 140.6, 122.5, 122.3, 108.9, 108.6, 104.9, 104.7, 60.8, 60.7, 60.6, 57.2, 40.3, 40.2, 34.8, 34.1, 33.9, 32.6, 32.4, 32.1, 31.8, 30.2, 30.0, 29.8, 29.1, 29.0, 28.7, 27.9, 25.4, 25.2, 24.6, 24.3, 22.8; IR (neat/NaCl) 3056, 3033, 2993, 2854, 1678, 1658, 1460, 1449, 1390, 1378, 1260, 1208, 1130, 933, 907, 734 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 225 (M^+ + 1, 13), 224 (8), 161 (44), 135 (10), 133 (8), 125 (10), 105 (10), 85 (8), 75 (100), 73 (12), 71 (20), 55 (8); HRMS (EI) *m/e* calcd for $C_{14}H_{24}O_2$ 224.1776, found 224.1752. Anal. Calcd for $C_{14}H_{24}O_2$: C, 75.25; H, 11.01. Found: C, 74.95; H, 10.78.

1,8*a*-Bis(dimethoxymethyl)decahydronaphthalene (28). To a 50-mL three-neck round bottom flask was added 0.250 g (1.1 mmol) of 1-(1-methoxy-(*E,Z*)-methylidene)-2-(5-methoxy-4-(*E,Z*)-pentenyl)cyclohexane, 4 mL of methanol, 36 mL of acetonitrile, 0.77 mL (11 mmol) of 2,6-lutidine, and 4.2 g (40 mmol) of lithium perchlorate. The resulting mixture was stirred in order to dissolve the electrolyte. Nitrogen was bubbled through the solution for 5 min and then the reaction started by passing 10 mA of current. The reaction was stopped after 214 C (2.0 F/mol) of charge had been passed. When complete, the reaction was diluted with water and ether and the layers were separated. The aqueous layer was extracted with ether and then the combined organic extracts were washed with brine solution, dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed through silica gel that was slurry-packed using a 1% triethylamine/pentane solution. Elution with 10% ether/pentane afforded 0.222 g (70%) of the cyclized products. The spectral data for the mixture of cis and trans isomers are as follows: ^{1}H NMR ($CDCl_3$/300 MHz) 4.85 (d, J = 1.2 Hz, 0.3 H), 4.77 (s, 0.3 H), 4.59 (s, 0.7 H), 4.50 (s, 0.7 H), 3.60, 3.55, 3.50, 3.38, 3.35, 3.32 (6 s, 1 H), 2.46 (dt, J_d = 13 Hz, J_t = 3 Hz, 0.7 H), 1.98 (br d, J = 12 Hz, 0.3 H), 1.86–1.60 (m, 5 H), 1.59–1.41 (m, 3 H), 1.40–1.41 (m, 7 H); ^{13}C NMR ($CDCl_3$/75 MHz) 111.5, 110.6, 108.5, 106.3, 60.2, 60.0, 58.6, 57.7, 56.7, 56.0, 54.7, 54.2, 52.4, 48.6, 44.6, 44.4, 43.2, 36.5, 35.1, 30.0, 29.6, 28.7, 28.6, 27.0, 26.8, 26.5, 23.3, 23.0, 22.9, 21.9, 20.3, 19.6; IR (neat/NaCl) 2927, 2861, 1289, 1449, 1384, 1187, 1148, 1113, 1068, 1018, 998, 914, 733 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 255 ($M^+ - OCH_3$, 11), 253 (2), 223 (9), 221 (3), 209 (5), 191 (8), 177 (3), 159 (3), 149 (9), 76 (11), 75 (100), 74 (12); HRMS (EI) *m/e* calcd for $C_{15}H_{27}O_3$ ($M^+ - OCH_3$) 255.1960, found 255.1982. Anal. Calcd for $C_{16}H_{30}O_4$: C, 67.10; H, 10.56. Found: C, 67.53; H, 10.66.

Acknowledgment. We thank the National Science Foundation (CHE-9023698) and Washington University for their generous support of this work. C.M.H. thanks the American Chemical Society Division of Organic Chemistry for a Graduate Student Fellowship (supported by Monsanto). We also gratefully acknowledge the Washington University High Resolution NMR Facility, partially supported by NIH grants RR02004, RR05018, and RR07155, and the Washington University Mass Spectrometry Resource Center, partially supported by NIHRR00954, for their assistance.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of all new compounds (46 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current mathead page for ordering information.

(14) Ellison, R. A.; Lukenbach, E. R.; Chie, C.-W. *Tetrahedron Lett.* 1975, 499.