tallographic symmetry. Careful electron-density studies around this site showed five small density peaks, but nothing which would make any chemical sense. We opted for treating these peaks as part of a highly disordered solvent system and assigned them as carbon atoms with occupancy factors appropriate to their peak heights. The figures were prepared with the aid of ORTEPII[26] and PLUTON.[27]

(26) Johnson, C. K. ORTEPII. Report ORNL-5138, Oak Ridge National Laboratory, TN, 1976.
(27) Spek, A. L. *PLUTON Molecular Graphics Program*; University of Utrech: The Netherlands, 1991.

Acknowledgment. We thank J. Phillips and G. B. Williams for assistance with the data collection of molecule 10. S.P. thanks M.U.R.S.T. for partial support of this work. G.F. thanks NSERC Canada for Grants in Aid of Research.

Supplementary Material Available: Table SI listing details of data collection, structure solution, and refinement for molecules 10, 7, and 6 (1 page). 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.

Concerning Attempts To Synthesize *out*-Bicyclo[4.4.4]tetradec-1-ene Derivatives

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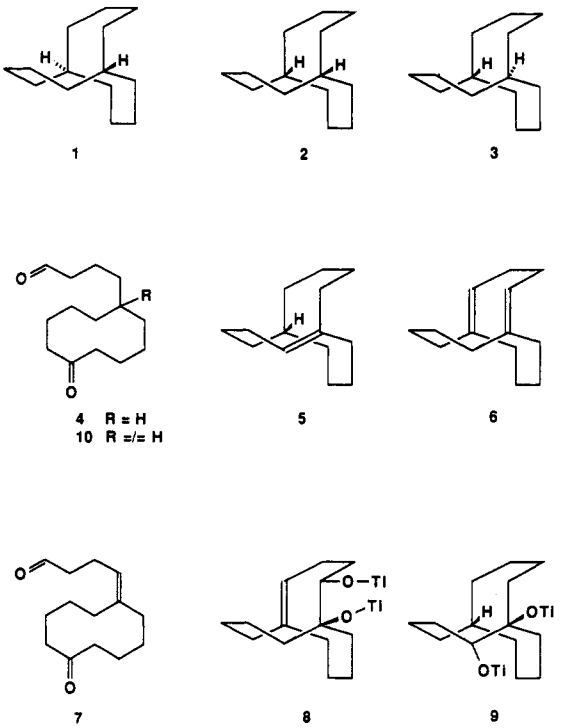
The keto aldehydes 4-[6-oxo-1-(tetrahydropyranyloxy)cyclodecyl]butanal (17), (*E*)-4-(6-oxocyclodec-1-enyl)butanal (24), and 4-(6-oxocyclodecylidene)butanal (7) have been synthesized. No bicyclo[4.4.4]tetradecadienes were found in the products from the zero-valent titanium reductive cyclization of compound 24. Instead, products arising from transannular reactions of the cyclodecyl ring system were isolated. 1,6-Divinylbicyclo[4.4.0]decane (32) was obtained from the reductive cyclization of keto enal 7. The most plausible route for its formation is through a Cope rearrangement of a bicyclo[4.4.4]tetradecene derivative, suggesting that an *out*-bicyclo[4.4.4]tetradecenylbistitanium pinacolate 8 intervened.

The strain inherent in bicyclo[4.4.4]tetradecane (1) was first suggested in a report[1] in 1974 and given a value derived from MM1 calculations. Further calculations have given rise to the suggestion[2,3] that potentially there are three different isomers of bicyclo[4.4.4]tetradecane, the in,out-isomer 2, the out,out-isomer 1, and the in,in-isomer 3, and that they are increasingly strained, in the order given. Calculations have also given rise to the suggestion[3] that the strain energies inherent in the corresponding bridgehead alkene derivatives are reduced over that of any of the saturated derivatives in this system. The term *hyperstable olefin* has been attached to such alkenes.

Conceptually, one could construct the bicyclo[4.4.4]-tetradecane skeleton by an intramolecular coupling reaction of an intermediate cyclodecyl derivative. In this context, the zero-valent titanium (Ti(0)) coupling reaction[4] of a keto aldehyde such as 4 is appealing since it offers a route to the saturated derivative by way of the bridgehead alkene derivative. The success of this approach to bicyclo[4.4.4]tetradecanes was clearly demonstrated by the synthesis of the in,out-isomer 2, via the in-alkene 5, by McMurry and Hodge.[5] With a more convergent approach than that first reported, it might be possible to delay introduction of the bridgehead hydrogens until after the cyclization had been effected. That is, it might be possible to synthesize a bicyclo[4.4.4]tetradecadiene such as 6.[6]



Reduction of such a diene would be expected to give the out,out-isomer 1. it is worth pointing out that the initial step, in the cyclization of a precursor such as 7, would give an out-alkene 8. The calculated strain[6b] energy for an out-alkene (182 kJ mol^{-1}) is lower than that calculated for an in,out-alkane (198 kJ mol^{-1}). An in,out-alkane intermediate 9 must form in the step leading to the in-alkene 5.

An alternative ploy, which might allow the synthesis of an out,out-derivative, is to put a substituent larger than hydrogen at the pro-bridgehead position in an intermediate

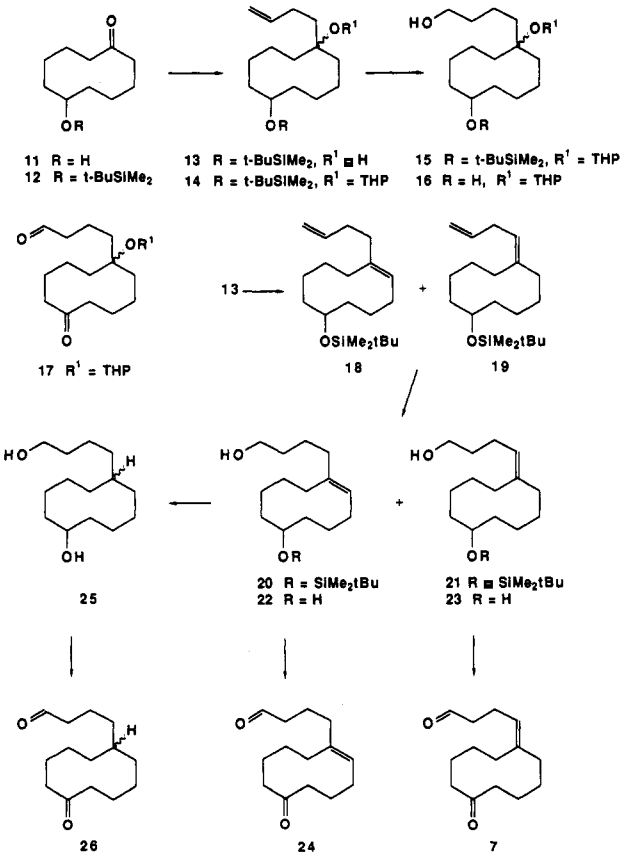
(1) Parker, W.; Tranter, R. L.; Watt, C. I. F.; Chang, L. W. K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 7121.
(2) Alder, R. W. *Acc. Chem. Res.* **1983**, *16*, 321.
(3) Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891.
(4) For a recent review see: McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513.
(5) McMurry, J. E.; Hodge, C. N. *J. Am. Chem. Soc.* **1984**, *106*, 6450.
(6) The strain energies associated with, at least, four of the five possible bridgehead dienes have been calculated and shown to be less, or comparable to, that calculated for the in-alkene 5: (a) Alder, R. W.; Arrowsmith, R. J.; Bryce, M. R.; Eastment, P.; Orpen, A. G. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1519. (b) McEwen, A. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 3951.

0022-3263/92/1957-7109$03.00/0

such as **10**. Because of the increased steric requirement of any such group, it is unlikely that this substituent will take up the in-position.

The Synthesis of the Key Intermediates. The side chains in the key intermediates such as **7** or **10** have a 1,6 relationship with respect to the formation of the new bridge from the preformed cyclodecane ring. Because of this, 6-hydroxycyclodecanone (**11**) was considered a suitable starting material for both sets of compounds. At that time, ketol **11**[7] was not available by an efficient route and an alternative synthesis was devised.[8]

Although ketol **11** exists in equilibrium with its hemiacetal isomer in solution,[7] it can be protected on the hydroxyl group, in high yield, as the *tert*-butyldimethylsilyl ether **12**. This cyclodecanone derivative appears to enolize readily, and it did not react satisfactorily with 3-butenylidenetriphenylphosphorane or with 3-butenylmagnesium bromide in ether. The required alcohol **13** could be obtained, however, in 60% yield as a mixture of cis and trans isomers, when the Grignard reaction was run in toluene[9] at −10 °C. The tertiary hydroxyl group could be protected[10] as the tetrahydropyranyl ether **14** and then hydroboration, followed by oxidation, of this alkene[11] gave a mixture of the alcohols **15**. Removal[12] of the silyl ether protecting group followed by oxidation[13,14] of the resulting diols **16** gave the required keto aldehyde **17**.



The mixture of alcohols **13** was dehydrated to a mixture of alkenyl isomers **18** and **19**, which could not be separated even by capillary GC. That this was an approximately 3:1 mixture of the endo and exo alkenes was indicated by the ^{1}H NMR spectrum of the mixture. A triplet at δ = 2.83 integrating for approximately 0.5 protons, relative to a broad multiplet at δ = 3.8 assigned to the methine proton on the carbon bearing the silyloxy group, is consistent with the doubly allylic methylene group of the exo isomer. Hydroboration,[11] followed by oxidation, of this mixture of dienes gave the primary alcohols **20** and **21**, but still the isomers could not be separated. Cleavage[12] of the silyl ether protecting group from these compounds gave the diols **22** and **23** which could be separated by repetitive flash chromatography. The major isomer eluted first. Although the stereochemistry about the endo double bond has not been established it is likely to be *E*, based on earlier work with cyclodecene systems.[15] Oxidation[13,14] of the major isomers **22** gave the keto enal **24**, and oxidation[14] of the minor isomer **23** gave the keto enal **7**.

Catalytic reduction of the mixture of enediols **22** and **23**, with hydrogen over platinum, gave the saturated diols **25** which have been reported earlier.[16] Oxidation of these diols gave the known[16] keto–al **26**.

Cyclization Reactions. The attempts to cyclize, by means of Ti(0) coupling reactions, any of the key intermediates synthesized produced a complex mixture of products, and so the decision was made to pursue only compounds whose molecular weight, as determined by combined GC–MS, was that of the desired cyclization product or close to it. As a consequence the only cyclizations worth discussing are those of the key intermediates **24** and **7**.

Initially, when no success was obtaied with the Ti(0) reactions, we sought to optimize the conditions by a repetition of the known[5] reaction to prepare *in*-bicyclo[4.4.4]tetradec-1-ene from keto aldehyde **26**. Very low yields (less than 5%) of the alkene were obtained until the detailed description of the conditions needed to perform these coupling reactions was available.[17] Even then we still did not realize the literature yield for this product but deemed that the 18% yield we did obtain was sufficient indication that we could attempt the unknown!

Keto enal **24** was added, by motor-driven syringe, to the Ti(0) under high dilution conditions over 20 h. The products from the reaction were separated into polar and nonpolar fractions by column chromatography, and the nonpolar fraction was analyzed by GC–MS to reveal a multitude of peaks. The material corresponding to two of these peaks was subsequently collected by preparative GC. A component having a high-resolution molecular ion corresponding to the formula $C_{14}H_{22}$ was isolated in yields varying from 1 to 4% between runs. A second component with a molecular ion consistent with the formula $C_{14}H_{24}$ was also obtained in yields of 1–3%.

The component $C_{14}H_{22}$, which has four double-bond equivalents, showed in the 300-MHz ^{1}H NMR spectrum one vinylic resonance as a multiplet at δ 5.29, three allylic resonances, as multiplets, at δ 2.26, 2.19 and 2.04, and two

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(8) Hamon, D. P. G.; Krippner, G. Y.; Pehlivanides, S. *J. Chem. Res.*, accepted for publication.
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(10) Mayashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772.
(11) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Synthese via Boranes*; Wiley and Sons: New York, 1975.
(12) Greene, T. W. *Protective Groups in Organic Syntheses*; John Wiley and Sons: New York, 1981.
(13) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647. Herscovici, J.; Antonakis, K. *J. Chem. Soc., Chem. Commun.* **1980**, 561.
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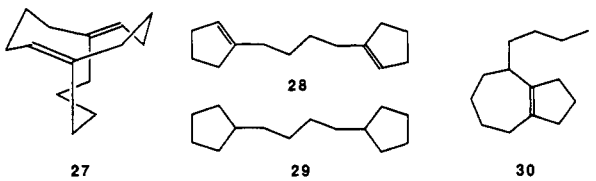
(15) Cope, A. C.; Ambros, D.; Ciganek, E.; Howell, C. F.; Jacura, Z. *J. Am. Chem. Soc.* **1959**, *81*, 3153. Cope, A. C.; Moore, P. T.; Moore, W. R. *J. Am. Chem. Soc.* **1959**, *81*, 3153. Zavada, J.; Svobuda, M.; Sicher, J. *Tetrahedron Lett.* **1966**, 1627.
(16) McMurry, J. E.; Leckta, T.; Hodge, C. N. *J. Am. Chem. Soc.* **1989**, *111*, 8867.
(17) McMurry, J. E.; Leckta, T.; Rico, J. G. *J. Org. Chem.* **1989**, *54*, 3748. We thank Professor McMurry for providing this procedure prior to publication.

other methylene resonances, a quintet at δ 1.82 and a multiplet at 1.41. These absorptions are in the ratio of 1:2:2:2:2:2, respectively. A ^{1}H COSY experiment showed that the vinylic resonance is coupled only with the allylic resonance at δ 2.26, the allylic resonances, at δ 2.26 and 2.19, are coupled with the quintet at δ 1.82, and the remaining allylic resonance, at δ 2.04, is coupled only to the resonance at δ 1.41. The ^{13}C NMR spectrum has seven resonances, two in the olefinic region, of which one is a singlet and the other a doublet in the off-resonance spectrum, and five in the aliphatic region, all of which are triplets in the off-resonance spectrum.

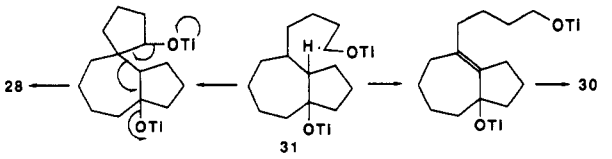
If, as assumed above, the stereochemistry about the double bond in the starting keto enal **24** is *E* then two isomeric $C_{14}H_{22}$ dienes, the *E,E*-isomer **27** and the *E,Z*-isomer, would be expected to form from an intramolecular coupling reaction. The *E,Z*-isomer can be excluded from consideration since it is an asymmetric molecule and should show 14 carbon resonances. The *E,E*-isomer, however, has a C_2 axis of symmetry and would be expected to show seven carbon resonances. Clearly the molecule that had been isolated showed spectral data consistent with the expected *E,E*-isomer **27**. The actual structure for this diene is, in fact, **28** which was totally unexpected. This only became clear after the following experiments.



The diene was hydrogenated at atmospheric pressure over platinum, and the reaction was complete in less than 12 h. It was clear that this diene hydrogenated more readily than the in-alkene **4**.[5,16] This was unexpected because it is considered that *hyperstable* alkenes will hydrogenate only with difficulty[3] and the stepwise reduction of the diene leads, in each step, to a molecule which is calculated to have increased strain. By high-resolution MS the product was shown to have the formula $C_{14}H_{26}$; that is, the addition of four hydrogens had occurred, and there are no vinylic resonances in the ^{1}H NMR spectrum or olefinic carbon resonances in the ^{13}C NMR spectrum. The ^{13}C NMR spectrum, in fact, shows five carbon resonances; the lowest field is a methine carbon the other four are methylene resonances. Alder predicts[18] that the most stable conformation of *out,out*-bicyclo[4.4.4]tetradecane is asymmetric; however, he also predicts that there are several conformations of similar energy available to the molecule and therefore it might well be expected that the molecule would exhibit D_3 symmetry and show only three carbon resonances. The possibility existed that the molecule was conformationally restricted and actually exhibiting C_3 symmetry, but with two of the expected six resonances fortuitously coincident. However, when an inverse-gated decoupling sequence, with a 10-s recycle time, was applied during the acquisition of the spectrum, it was found that the integrals for the resonances at δ 40.20, 36.31, 32.75, 29.08, and 25.21 were in the ratio of 1:1:2:1:2. This observation excludes C_3 symmetry.

The spectroscopic data are consistent[18b] also with 1,4-dicyclopentylbutane (**29**). This compound has been reported,[19] but the synthesis given is not straightforward.

Scheme I



Scheme II

However, ^{13}C NMR data provided are very similar to the data which had been obtained for the saturated compound above. If this is indeed the structure for the saturated compound then the question arises as to whether the precursor diene has the structure **28** or had rearrangement, from the structure **27**, occurred on contact with the platinum catalyst prior to hydrogenation. The spectroscopic data do not allow differentiation of the two possibilities. Conclusive evidence that the saturated compound is 1,4-dicyclopentylbutane (**29**) and that the diene has structure **28** came recently from an independent synthesis[20] of the hydrocarbon **29** which proceeds through a mixture of 1-cyclopentylidene-4-cyclopent-1-enylbutane and 1,4-dicyclopent-1-enylbutane (**28**).

This unexpected result clearly begs an explanation. The other component isolated from the preparative GC perhaps gives a clue to the process whereby this comes about. Although this compound has not been fully characterized, the evidence there is points clearly to structure **30** (or a double-bond isomer). The formula $C_{14}H_{24}$ requires three double-bond equivalents. The ^{13}C NMR spectrum shows 14 carbon resonances, two of which are olefinic. The ^{1}H NMR spectrum shows no vinylic protons, there is a triplet at δ 0.87 consistent with the methyl group of the side chain, and there appears to be seven allylic protons. The base peak in the MS at m/z 135 is consistent with the loss of the side chain. Cyclodecyl compounds are well-known to undergo transannular reactions,[21] and the formation of both compounds **28** and **30** may well arise because of this. A transannular reaction in the initial pinacol reduction would give rise to an intermediate diradical[22] **31** (see Scheme I) which could well react further in the two ways depicted eventually leading to the two products observed.[23]

When a Ti(0) coupling reaction was attempted on the isomeric keto enal **7**, followed by a similar workup, a component with a molecular weight of 190 was present in the GC–MS (about 15% yield by internal standard) which was isolated, in 8% yield by preparative GC. This component proved to be 1,6-divinylbicyclo[4.4.0]decane (**32**) by comparison of the spectral data with the reported

(18) (a) Alder, R. W. *Tetrahedron* **1990**, *46*, 683. (b) We thank Dr. Alder for stimulating discussions and for his role as "devils advocate" in pointing out this possibility.

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(20) Ripper, J. A. Undergraduate Honors thesis, University of Adelaide, 1991. The dienes were prepared by dehydration of the diol obtained from the reaction of butanebis(1,4-magnesium bromide) with cyclopentanone.

(21) Cope, A. C.; Martin, M. M.; McKervey, M. A. *Q. Rev., Chem. Soc.* **1966**, *20*, 119.

(22) Dams, R.; Malinowski, M.; Westdorp, I.; Giese, H. J. *J. Org. Chem.* **1982**, *47*, 248.

(23) A reviewer has suggested that the diene **28** could have arisen from the highly reactive diene **27** by a (2 + 2) cycloaddition, to a cyclobutane, followed by a retro (2 + 2). However, as we understand it, this would have to be a nonconcerted process since the geometry necessary for a ($2\pi s + 2\pi a$) process is not attainable and, therefore, it would not be especially favored.

values[24] and by direct comparison of their ^{13}C NMR spectra. The divinyldecalin **32** had been prepared in order to use it as a precursor in a Cope rearrangement to *meso*-bicyclo[4.4.4]tetradec-1,5-diene (**6**). The bicyclotetradecadiene was not obtained by this route, and it can be concluded that the position of equilibrium lies too much in favor of the divinyldecalin.[6a,24]

What is not clear in the above titanium reaction is if bicyclo[4.4.4]tetradeca-1,5-diene (**6**), or its stereoisomer, had formed. No NMR analysis was tried on the crude reaction product from the titanium reaction which is done at 80 °C. Instead, the product was isolated by evaporative distillation and preparative GC (175 °C). However, it would seem clear that, to have formed the 1,6-divinyldecalin **32**, the *out*-bicyclo[4.4.4]tetradecene derivative **8** must have formed. It is possible that this titanium-complexed pinacol derivative may have rearranged to the divinyldecalin directly in a reductive Cope-like process (see Scheme II).

Although it seems likely that an *out*-bicyclo[4.4.4]tetradecene derivative intervened in the formation of the divinyldecalin **32** whether the parent compound can be isolated has yet to be demonstrated.

Experimental Section

General. Flash chromatography[25] was carried out using Merck Keiselgel 60 (230–400 mesh). Short column chromatography[26] was done with Merck Keiselgel HF_{254}. Analytical TLC was performed using Merck DC-Alufolein Keiselgel $60F_{254}$ and visualized using an ethanolic solution of phosphomolybdic acid (4% w/v). Drying and other purification of organic solvents were accomplished by standard laboratory procedures;[27] in addition, DME was twice distilled from potassium. Nitrogen was used as carrier gas, with FID, for analytical GC. IR spectra were recorded as neat films unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded at 300.1 MHz and 75.4 MHz respectively as solutions in $CDCl_3$. FAB spectra were recorded on samples either neat or in a glycerol matrix.

6-[(*tert*-Butyldimethylsilyl)oxy]cyclodecan-1-one (12). An anhydrous solution of 6-hydroxycyclodecan-1-one (**11**)[8] (3.33 g, 19.5 mmol), TBDMS chloride (5.01 g, 33.24 mmol), and DMAP (0.85 g, 7.0 mmol) in CH_2Cl_2/triethylamine (4:1, 40 mL) was stirred under N_2 for 48 h. The reaction was diluted with CH_2Cl_2 (50 mL) and then washed first with HCl (dilute, 20 mL) and then with water (3 × 20 mL) and finally $NaHCO_3$ (saturated 20 mL). The combined organic fractions were dried and concentrated to give a yellow oil which was distilled (110 °C/0.01 mmHg) in a Kugelrohr apparatus to give the ketone **12** (5.28 g, 18.6 mmol, 95%) as a clear colorless oil which was pure enough for subsequent reactions; ν_{max} 1706 cm^{-1} s; ^1H (60 MHz) NMR δ 3.64 (br m, 1 H), 2.27–2.57 (m, 4 H), 1.25–1.98 (m, 12 H), 0.83 (s, 9 H), 0.05 (s, 6 H); ^{13}C (22.1 MHz) NMR δ 214.07, 70.1, 41.9, 33.4, 25.7, 23.3, 22.3, 17.8, −4.7; MS m/z (FAB) 283 $(M - H)^+$, 227 $(M - C_4H_9)^+$; (EI) m/z 227 $(M - C_4H_9)^+$ (100), found 227.1475, $C_{12}H_{23}O_2Si$ $(M - C_4H_9)^+$ requires 227.1467. A small sample purified by chromatography and then distillation crystallized to a waxy solid, mp 21–23 °C.

1-(3-Butenyl)-6-[(*tert*-butyldimethylsilyl)oxy]cyclodecan-1-ols (13). A solution of 3-butenylmagnesium bromide in ether (55 mL) was prepared under N_2 from 4-bromobut-1-ene (8.18 g, 60.6 mmol) and magnesium (2.13 g, 0.091 g atoms). Dry toluene (100 mL) was added to the Grignard solution, the ether was removed by fractional distillation, and then a further aliquot of toluene (150 mL) was added. The Grignard solution was cooled to −10 °C, and a solution of ketone **12** (8.6 g, 30.3 mmol) in toluene (20 mL) was added slowly to the Grignard solution. The reaction was allowed to warm to rt overnight. The reaction was poured into NH_4Cl (saturated, 300 mL) and extracted into ether (3 × 150 mL). The combined organic fractions were washed with $NaHCO_3$ (saturated, 50 mL) and brine (100 mL) and dried. Removal of the solvents gave a mixture of products that was separated by flash chromatography (1:9 ether/hexanes) to give, in order of elution, ketone **12** (2.58 g, 10 mmol, 30%), an isomeric mixture of the alcohols **13** (6.19 g, 20 mmol, 60%) as a clear colorless oil [ν_{max} 3375 br s, 3060 m, 1640 cm^{-1} s; ^1H NMR δ 5.85 (ddt, J = 17, 10.6, 6.7 Hz, 1 H), 5.04 (br d, J = 17 Hz, 1 H), 4.94 (br d, J = 10.6 Hz, 1 H), 3.87 (m, 1 H), 2.16 (dt, J = 5.0, 6.7 Hz, 2 H), 1.79–1.34 (m, 20 H), 0.87 (s, 9 H), 0.05 (s, 6 H); ^{13}C NMR δ 139.25, 114.29, 114.24, 75.92, 75.88, 72.14, 72.07, 40.22, 33.49, 33.33, 31.90, 31.34, 27.47, 25.84, 21.97, 21.77, 21.23, 21.03, 18.1, −4.76; MS m/z 283 (3%) $(M - C_4H_9)^+$, 75 (100), found 283.2104, $C_{16}H_{31}O_2Si$ $(M - C_4H_9)^+$ requires 283.2093. $C_{20}H_{40}O_2Si$ requires: C, 70.52; H, 11.84. Found: C, 70.35; H, 11.79.] and **1-[(*tert*-butyldimethylsilyl)oxy]cyclodecan-6-ol** (0.6 g, mmol, 7%) as a mixture of isomers: ν_{max} 3320 cm^{-1} br s; ^1H NMR δ 3.92 (m, 1 H), 3.83 (m, 1 H), 1.55 (m, 16 H), 0.85 (s, 9 H), 0.03 (s, 6 H); ^{13}C NMR δ 72.06, 71.76, 71.31, 71.05, 32.75, 32.36, 31.78, 31.65, 25.89, 21.94, 21.75, 18.12, −4.58, −4.71; MS m/z 269 (3) $(M - OH)^+$, 229 (100); found 269.2290, $C_{16}H_{33}OSi$ $(M - OH)^+$ requires 269.2300.

4-[6-[(*tert*-Butyldimethylsilyl)oxy]-1-(tetrahydropyranyloxy)cyclodecyl]but-1-ene (14). PPTS[10] (0.24 g, 0.95 mmol) was added to an anhydrous solution of the alcohols **13** (3.24 g, 9.5 mmol) in dihydropyran (4.8 g, 57 mmol) and stirred for 36 h under N_2. The reaction was diluted with ether (20 mL) and washed with brine (15 mL), and then the aqueous phase was extracted with ether (20 mL) and the combined organic phases dried and concentrated to give a clear colorless oil. Purification by flash chromatography (1:4 ether/hexanes) gave a mixture of the isomeric alkenes **14** (3.71 g, 8.7 mmol, 92%) as a colorless viscous oil for which satisfactory analytical data were not obtained: ν_{max} 3075 m, 1640 cm^{-1} s; ^1H NMR δ 5.8 (ddt, J = 17, 10, 6 Hz, 1 H), 4.99 (dd, J = 17, 1.5 Hz, 1 H), 4.90 (dd, J = 10, 1.5 Hz, 1 H), 4.70 (m, 1 H), 3.95 (m, 1 H), 3.84 (m, 1 H), 3.44 (m, 1 H), 2.20 (m, 1 H), 2.00 (m, 1H), 1.87–1.33 (m, 24 H), 0.88 (s, 9 H), 0.03 (s, 6 H); ^{13}C NMR δ 139.5, 139.4, 113.75, 93.17, 92.99, 81.62, 72.37, 72.25, 63.64, 63.40, 36.74, 36.43, 32.52, 32.34, 31.78, 31.69, 31.52, 31.28, 30.69, 30.58, 27.45, 25.85, 25.70, 25.45, 22.53, 22.44, 22.26, 22.20, 21.06, 20.96, 20.91, 20.74, 18.09, −4.75; MS m/z 424 (<1) (M^+), 323 (67) $(M - C_5H_9O_2)^+$, 85 (100); found 367.2658, $C_{21}H_{39}O_3Si$ $(M - C_4H_9)^+$ requires 367.2668, found 323.2779, $C_{20}H_{39}OSi$ $(M - C_5H_9O_2)^+$ requires 323.2770.

4-[6-[(*tert*-Butyldimethylsilyl)oxy]-1-(tetrahydropyranyloxy)cyclodecyl]butan-1-ol (15). A solution of the THP ethers **14** (1.56 g, 3.67 mmol) in THF (5 mL) was added slowly to disiamylborane[11] (9.4 mmol) in THF (7.3 mL) at −10 °C under N_2; when addition was complete the reaction mixture was allowed to warm to rt and stirred for 12 h. Excess disiamylborane was quenched with water. NaOH (3 M, 4.4 mL) was added to the reaction mixture, and aqueous H_2O_2 solution (30% w/w, 4.4 mL, 42.4 mmol) was added at a rate to maintain the temperature below 50 °C. The mixture was then heated at 50 °C for 4 h. Ether (10 mL) was added, and the aqueous phase was saturated with solid NaCl. The organic phase was separated, and the aqueous phase was extracted with ether (2 × 15 mL). The combined organic phases were washed with brine (15 mL) and dried, and then the solvents were removed to give a colorless oil. Separation of the components by short column chromatography (100% hexanes to 100% ether by 5% increments) gave a mixture of isomeric alcohols **15** (1.51 g, 3.41 mmol, 93%) as a colorless oil: ν_{max} 3400 cm^{-1} br s; ^1H NMR δ 4.70 (m, 1 H), 3.96 (m, 1 H), 3.84 (m, 1 H), 3.62 (m, 2 H), 3.44 (m, 1 H), 1.88–1.29 (methylene envelope), 0.88 (s, 9 H), 0.04 (s, 6 H); ^{13}C NMR δ 93.50, 93.37, 81.99, 72.34, 72.21, 63.86, 63.67, 61.93, 36.43, 36.24, 32.62, 32.44 (br), 32.29, 31.64, 31.45, 30.74, 30.48, 25.89, 25.44, 22.70, 22.27, 21.04, 20.59, 18.43, 18.12, −4.70; MS m/z (FAB) 425 (8) $[(M + H) - H_2O]^+$, 95 (100). $C_{25}H_{50}O_4Si$ requires: C, 67.82; H, 11.38. Found: C, 67.9; H, 11.36.

4-[6-Hydroxy-1-(tetrahydropyranyloxy)cyclodecyl]butan-1-ol (16). A solution of tetrabutylammonium fluoride in THF (1 M, Aldrich, 3.0 mL, 3.0 mmol) was added to the THP ether **15** (0.47 g, 1.07 mmol) and left to stir under N_2 for 5 days. The mixture was diluted with ethyl acetate/hexane (3:2, 3 mL), and

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the components were separated on silica gel (70 g) (gradient elution of 60–100% ethyl acetate/hexanes) to give, in order of elution, THP ether **15** (60 mg, 0.14 mmol 13%) and the isomeric diols **16** (289 mg, 0.88 mmol, 82%) as a colorless oil for which satisfactory analytical data were not obtained: ν_{max} 3360 cm^{-1} br s; ^1H NMR δ 4.68 (m, 1 H), 3.95–3.8 (overlapping m, 2 H), 3.61 (m, 2 H), 3.44 (m, 1 H), 1.23–1.89 (methylene envelope and OH); ^{13}C NMR δ 90.35, 81.61, 71.69, 71.63, 63.72, 61.66, 36.37, 36.12, 32.49, 32.36, 32.23, 31.91, 31.39, 30.74, 30.49, 25.37, 22.71, 22.17, 22.14, 20.89, 20.33, 18.39; MS *m/z* (FAB) 329 $(M + H)^+$, 311, 227 $(M - C_5H_9O_2)^+$; (EI) *m/z* 227 (16) $(M - C_5H_9O_2)^+$, 85 (100); found 227.2012, $C_{14}H_{27}O_2$ $(M - C_5H_9O_2)^+$ requires 227.2011.

4-[6-Oxo-1-(tetrahydropyranyloxy)cyclodecyl]butanal (17). Method 1.[13] Anhydrous CH_2Cl_2 (15 mL) was added to PCC (0.5 g, 2.3 mmol), powdered 4-Å sieves (Aldrich, 0.59 g), and anhydrous sodium acetate (0.193 g, 2.3 mmol), and the suspension was stirred under N_2 for 20 min. A solution of the diol **16** (0.189 g, 0.57 mmol) in CH_2Cl_2 (7 mL) was added slowly, and the reaction was stirred for 20 min. Anhydrous ether (20 mL) was added, and the reaction was stirred for a further 30 min. The reaction mixture was filtered through a pad of Florisil, the residue was washed with ether, and the filtrate was concentrated to give an orange oil. The principal component of this oil (R_f 0.17) was isolated by flash chromatography (1:4 ethyl acetate/hexanes) to give the keto aldehyde **17** (0.121 g, 0.37 mmol, 65%) as a colorless oil for which satisfactory analytical data were not obtained: ν_{max} 2724 w, 1725 s, 1707 cm^{-1} s; ^1H NMR δ 9.69 (t, *J* = 1.9 Hz, 1 H), 4.56 (m, 1 H), 3.88 (m, 1 H), 3.38 (m, 1 H), 2.51 (m, 4 H), 2.32 (td, *J* = 7.1, 1.9 Hz, 2 H), 1.16–1.9 (methylene envelope); ^{13}C NMR δ 214.81, 202.77, 93.49, 80.96, 63.61, 44.01, 42.51, 35.79, 32.10, 31.84, 31.52, 25.23, 23.86, 20.78, 20.13, 20.00, 15.79; MS *m/z* 324 (<1) M^+, 85 (100); found 324.2299, $C_{19}H_{32}O_4$ requires 324.2301.

Method 2.[14] A solution of anhydrous DMSO (0.22 mL, 3.1 mmol) in CH_2Cl_2 (2 mL) was added slowly to a stirred solution of oxalyl chloride (1.6 mmol) in CH_2Cl_2 (4 mL) at −50 °C under N_2. The mixture was stirred for 2 min, and then to it was slowly added a solution of the diol **16** (140 mg, 0.43 mmol) in CH_2Cl_2 (1 mL). After 15 min, triethylamine (1 mL, 7.03 mmol) was added slowly. The reaction was stirred at −50 °C for 5 min and then warmed to rt and stirred for a further 30 min. The reaction was diluted with CH_2Cl_2 (5 mL) and poured into water (5 mL) which was back-extracted with CH_2Cl_2 (2 × 5 mL). The combined organic phases were washed with $NaHCO_3$ (saturated, 5 mL) and then dried and concentrated. The keto aldehyde **17** (100 mg, 0.31 mmol, 72%) was isolated by flash chromatography as described above.

(*E*)-4-[6-[(*tert*-Butyldimethylsilyl)oxy]cyclodec-1-enyl]but-1-ene (18) and 4-[6-[(*tert*-Butyldimethylsilyl)oxy]cyclodecylidene]but-1-ene (19). A solution of $SOCl_2$ (1.4 mL, 19.1 mmol) in pyridine (7 mL) was slowly added to a stirred solution of the tertiary alcohols **13** (5.22 g, 15.3 mmol) in pyridine at −10 °C under N_2. After 15 min the reaction was diluted with ether (100 mL) and then poured into $NaHCO_3$ solution (saturated, 65 mL). The aqueous phase was extracted with ether (3 × 100 mL), the combined organic phases were washed with brine (50 mL) and then dried, and the solvents were removed. The crude residue was purified by flash chromatography (hexanes) to give an inseparable mixture of the dienes **18** and **19** (4.63 g, 14.35 mmol, 94%): ν_{max} 3060 m, 1640 cm^{-1} s; ^1H NMR δ 5.83 (ddt, *J* = 17.5, 10, 1.9 Hz, 1 H), 5.17 (br t, *J* = 8.4 Hz, 1 H), 5.03 and 4.94 (br AB, *J* = 17.5, 10 Hz, 2 H), 3.8 (m, 1 H), 2.83 (t, *J* = 8 Hz, 0.5 H), 1.8–2.4 (allylic), 1.2–1.8 (methylene envelope), 0.88 (s, 9 H), 0.04 (s, 6 H); ^{13}C NMR δ 138.91, 137.62, 137.29, 125.71, 122.71, 114.24 br, 71.90, 71.56, 35.01, 33.83, 33.67, 32.53, 32.31, 32.21, 31.19, 29.7 br, 26.18, 26.01, 25.92, 25.42, 25.11, 24.36, 23.02, 22.07, 20.21, 19.28, 18.18, −4.6, −4.7; MS *m/z* 321 (0.8) $(M - H)^+$, 265 $(M - t\text{-}Bu)^+$, 75 (100); found 265.1969, $C_{16}H_{29}OSi$ $(M - C_4H_9)$ requires 265.1988. $C_{20}H_{38}OSi$ requires: C, 74.46; H, 11.87. Found: C, 74.39; H, 11.82.

(*E*)-4-[6-[(*tert*-Butyldimethylsilyl)oxy]cyclodec-1-enyl]butan-1-ol (20) and 4-[6-*tert*-Butyldimethylsilyl)oxy]cyclodecylidene]butan-1-ol (21). A solution of the dienes **18** and **19** (1.56 g, 4.8 mmol) in THF (3 mL) was added rapidly to a stirred solution of disiamylborane (6.6 mmol) in THF (7 mL) at 0 °C under N_2. After 3 h the reaction was quenched with water and worked up in the usual way. Flash chromatography (1:9 ethyl acetate/hexanes) was used to isolate, as an inseparable mixture (one component by TLC), the alcohols **20** and **21**: ν_{max} 3300 br s, 1645 cm^{-1} w; ^1H NMR δ 5.15 (t, *J* = 9.0 Hz, 1 H), 3.78 (m, 1 H), 3.62 (t, *J* = 6.0 Hz, 2 H), 1.8–2.4 (m, 6 H), 1.19–1.78 (methylene envelope), 0.88 and 0.87 (2 × s, 9 H), 0.04 and 0.03 (2 × s, 6 H); ^{13}C NMR δ 138.39, 138.14, 125.59, 124.90, 71.86, 71.53, 62.83, 62.68, 35.29, 33.78, 33.70, 33.21, 32.79, 32.58, 31.16, 29.66 br, 26.10, 25.87, 25.78, 25.34, 25.11, 24.31, 24.04, 22.98, 22.40, 20.22, 19.24, 18.12, −4.65, −4.73; MS *m/z* 340 (1) M^+, 75 (100); found 340.2812, $C_{20}H_{40}O_2Si$ requires 340.2798.

(*E*)-4-(6-Hydroxycyclodec-1-enyl)butan-1-ol (22) and 4-(6-Hydroxycyclodecylidene)butan-1-ol (23). A mixture of silyloxy enols **20** and **21** (1.26 g, 3.67 mmol) in THF (14 mL) was added to acetic acid/water (3:1, 56 mL), and the solution was stirred under N_2 for 36 h. The reaction mixture was poured into CH_2Cl_2 (250 mL) and water (75 mL), the organic layer was washed with water (2 × 75 mL) and saturated $NaHCO_3$ solution (50 mL) and then dried, and the solvent was removed. The mixture of diols **22** and **23** (1.12 g, 4.95 mmol, 86%) was isolated as a clear oil by way of flash chromatography (1:1 ethyl acetate/hexanes). The diols were separated by repetitive flash chromatography (9:11 ethyl acetate/hexanes) to give in order of elution diol **22** (one component by TLC) [ν_{max} 3345 br s, 1655 cm^{-1} w; ^1H NMR δ 5.13 (t, *J* = 8.2 Hz, 1 H), 3.83 (m, 1 H), 3.63 (t, *J* = 6.2 Hz), 2.26 (m, 2 H), 2.14 (s, OH), 2.07 (m, 2 H), 1.97 (q, *J* = 7.5 Hz, 2 H), 1.24–1.79 (methylene envelope); ^{13}C NMR δ 138.40, 125.26, 71.24, 62.70, 35.21, 33.40, 32.49, 29.51, 25.77, 24.21, 24.01, 23.10, 18.97; MS *m/z* = 226 (0.5) (M^+), 81 (100); found 226.1941, $C_{14}H_{26}O_2$ requires 226.1933] and diol **23** (essentially one component by TLC): ν_{max} 3345 br s, 1655 cm^{-1} w; ^1H NMR δ 5.12 (t, *J* = 7.2 Hz, 1 H), 3.77 (m, 1 H), 3.59 (t, *J* = 6.9 Hz, 2 H), 1.9–2.3 (m, 8 H), 1.2–1.9 (methylene envelope); ^{13}C NMR δ 137.82, 125.01, 70.59, 62.14, 33.59, 33.07, 32.68, 32.57, 31.06, 24.94, 24.79, 24.21, 22.59, 19.87; MS *m/z* = 168 (61) $(M - C_3H_6O)^+$, 153 (100); found 168.1507, $C31_1H_{20}O$ $(M - C_3H_6O)^+$ requires 168.1515.

(*E*)-4-(6-Oxocyclodec-1-enyl)butanal (24). A suspension of PCC (0.827 g, 3.84 mmol), sodium acetate (fused, 84 mg, 1.02 mmol), and powdered 4-Å molecular sieves (1.013 g, Aldrich) in CH_2Cl_2 (13 mL) was stirred under N_2 for 1.5 h, and then a solution of the enediol **22** (172 mg, 0.76 mmol) in CH_2Cl_2 (5 mL) was added slowly. After 10 min the reaction was diluted with anhydrous ether (15 mL) and stirred for 15 min before it was filtered through a pad of Florisil. The residue was rinsed with ether (240 mL), and the solvents were removed to leave a viscous brown oil. The principal component was isolated by flash chromatography (3:7 ethyl acetate/hexanes) to give the keto aldehyde **24** (121 mg, 0.54 mmol, 70%) as a clear oil (one component by TLC): ν_{max} 2716 m, 1724 s, 1704 cm^{-1} s; ^1H NMR δ 9.72 (t, *J* = 1.95 Hz, 1 H), 5.13 (t, *J* = 8.5 Hz, 1 H), 2.2–2.5 (td, *J* = 7.3, 1.9 Hz, overlapping m, 6 H), 1.8–2.2 (m, 6 H), 1.4–1.8 (m, 8 H); ^{13}C NMR δ 213.46, 201.61, 138.46, 124.95, 45.56, 42.71, 34.11, 33.71, 25.44, 24.60, 23.24, 22.39, 20.59, 19.35; MS *m/z* = 222 (2) M^+, 67 (100); found 222.1613, $C_{14}H_{22}O_2$ requires 222.1620; found C 75.21, H 9.64, $C_{14}H_{22}O_2$ requires C 75.63, H 9.97.

4-(6-Oxocyclodecylidene)butanal (7). A solution of diol **23** (150 mg, 0.66 mmol) in CH_2Cl_2/DMSO (1:1, 1.5 mL) was added to the reagent prepared from oxalyl chloride (0.29 mL, 3.3 mmol) in CH_2Cl_2 (9 mL) and DMSO (0.5 mL, 7.0 mmol) at −60 °C. After 1 h triethylamine (2.3 mL, 16.5 mmol) was added and the reaction worked up as described for compound **17** above. The major component of the crude product was separated by flash chromatography (1:4 ethyl acetate/hexanes) to give the keto aldehyde **7** (77 mg, 0.35 mmol, 53%) as a clear oil (one component by TLC): ν_{max} (CCl_4) 2716 m, 1730 s, 1706 cm^{-1} s; ^1H NMR δ 9.78 (t, *J* = 1.5 Hz, 1 H), 5.13 (t, *J* = 6.9 Hz, 1 H), 2.51 (m) with 2.44 (m) and 2.35 (m) (total 6 H), 2.14 (m, 2 H), 1.8–2.0 (m, 4 H), 1.5–1.8 (m, 6 H); ^{13}C NMR δ 214.36, 202.13, 139.63, 121.71, 43.81, 43.61, 37.02, 30.81, 30.54, 24.53, 23.30, 23.07, 22.14, 20.52; MS *m/z* = 222 (1) $(M)^+$, 55 (100); found 222.1615, $C_{14}H_{22}O_2$ requires 222.1620.

4-(6-Hydroxycyclodecyl)butan-1-ol (25). A mixture of the enediols **22** and **23** (1.23 g, 5.4 mmol) in ethyl acetate (10 mL) was hydrogenated at atmospheric pressure over PtO_2 (245 mg) for 3 days. The reaction was passed through a short plug of Celite and the residue washed with ethyl acetate. The crude concentrate was separated by flash chromatography (3:7 ethyl acetate/hexanes) to give, in order of elution, isomers of **4-(6-hydroxycyclodecyl)butan-1-yl acetate** (0.242 g, 0.89 mmol, 16%) as a

clear oil [ν_{max} 3410 s br, 1738 s, 1725 cm^{-1} sh; ^1H NMR δ 4.07 (t, J = 6.5 Hz, 2 H), 3.95 (m, 1 H), 2.88 (br s, OH), 2.05 (s, 3 H), 1.15–1.87 (methylene envelope)] and the diol **25** (0.893 g, 3.9 mmol, 72%) as an oil whose spectral data were similar to those reported in the literature:[16] ^{13}C NMR δ 71.8, 70.6, 62.5, 36.8, 36.2, 35.9, 34.8, 33.3, 32.9, 32.4, 30.2, 29.0, 23.6, 22.5, 22.0.

4-(6-Oxocyclodecyl)butanal (26). This compound was prepared from the diols **25** (132 mg, 0.58 mmol) essentially by the method described[16] except that it was further purified by flash chromatography (3:7 ethyl acetate/hexanes) to give an oil (91 mg, 0.41 mmol, 71%) with spectral properties identical to those reported.

Reaction of (*E*)-4-(6-Oxocyclodec-1-enyl)butanal (24) with Zero-Valent Titanium. A well-stirred suspension of $TiCl_3 \cdot (DME)_{1,5}$[17] (10.37 g, 35.8 mmol) and zinc–copper couple[4] (6.42 g, 98.16 mmol) in DME (280 mL) was refluxed under an atmosphere of argon for 4 h and then cooled to 80 °C. A solution of the keto enal **24** (200 mg, 0.9 mmol) in DME (26 mL) was added over a period of 20 h by way of a syringe pump; the suspension was stirred for a further 12 h and then cooled to rt. The mixture was diluted with degassed, anhydrous pentane (200 mL) and then filtered through a pad of Florisil under a positive pressure of argon. The residues were washed with pentane (250 mL), and then the combined filtrates were concentrated to a volume of 2 mL by distillation at atmospheric pressure. Final traces of solvent were removed at 0 °C under reduced pressure. The residue was separated by flash chromatography (100% hexanes to 100% ethyl acetate) into a nonpolar fraction (97 mg) and an intractable mixture of polar components (66 mg). The nonpolar fraction was analyzed by GC (SCOT column OV101, 0.5 mm × 40 m, at 170 °C/45 kPa) and GC–MS, which resolved, in order of elution, four major volatile components with corresponding m/z 178, 192, 190, 206 in the ratio 0.7:1:1:1.3. The use of tetradecane as an internal standard indicated that the component m/z 190 had been produced in 5.5% yield. The components were separated by preparative GC (20% OV101 on Varaport 30, 80–100 mesh, 6 mm × 2 m at 180 °C with argon as carrier gas) using liquid nitrogen cooled traps to condense the column effluent. 1,4-Dicyclopentenylbutane (**28**) (6 mg, 31.5 mmol, 3.5%) was isolated as a clear oil (mainly one component by injection on SCOT column, OV101, 50 m): ^1H NMR δ 5.29 (m, 2 H), 2.26 (m) and 2.19 (m, 8 H), 2.04 (br s, 4 H), 1.82 (quintet, J = 7.2 Hz, 4 H), 1.41 (m, 4 H); ^{13}C NMR δ 144.93 (s), 123.07 (d, $^1J_{C-H}$ = 157.7 Hz), 35.08 (t), 32.42 (t), 31.07 (t), 27.70 (t), 23.43 (t); MS m/z = 190 (15) (M^+), 161 (3), 148 (3), 147 (3), 135 (4), 133 (5), 121 (33), 108 (93), 93 (77), 79 (85), 69 (100), 67 (81), 55 (21), 53 (28); found 190.1717, $C_{14}H_{22}$ requires 190.1721. Also isolated was the bicyclic alkene **30** or an isomer (mainly one component by injection on SCOT column, OV101, 50 m) (4.6 mg, 24 mmol, 2.5%): ^1H NMR δ 2.29 (m, 4 H), 2.08 (m, 3 H), 1.2–1.75 (m, 14 H), 0.87 (t, J = 6.9 Hz, 3 H); ^{13}C NMR δ 141.10, 136.39, 40.19, 39.54, 38.64, 31.71, 30.67, 30.29, 29.25, 27.58, 25.95, 22.98, 22.39, 14.12; MS m/z 192 (13) (M^+), 135 (100).

Hydrogenation of the Diene 28. A suspension of the diene **28** (6 mg, 32 mmol) and platinum oxide (16 ng) in ether (4 mL) were stirred under an atmosphere of hydrogen for 12 h. The reaction was filtered through a plug of Celite, and the residues were washed with ether. The solvents were removed from the filtrate to give 1,4-dicyclopentylbutane (**29**) (6 mg, 30 mmol, 94%) which coeluted with the diene **28** on GC (vide supra): ^1H NMR δ 1.71 (m, 6 H), 1.53 (m) and 1.48 (m, 8 H), 1.25 (m, 8 H), 1.03 (m, 4 H); ^{13}C NMR δ 40.20 (d, 2 C), 36.31 (t, 2 C), 32.75 (t, 4 C), 29.08 (t, 2 C), 25.21 (t, 4 C) (lit.[19] ^{13}C NMR δ 40.9 (d), 37.0 (t), 33.4 (t), 29.8 (t), 25.9 (t)); MS m/z 194 (11) (M^+), 82 (100); found 194.2022, $C_{14}H_{26}$ requires 194.2034.

Reaction of 4-(6-Oxocyclodecylidene)butanal (7) with Zero-Valent Titanium. A well-stirred suspension of $TiCl_3 \cdot (DME)_{1,5}$[17] (4.6 g, 13.6 mmol) and zinc–copper couple[4] (2.89, 44.2 mmol) in DME (115 mL) was refluxed for 4 h under an atmosphere of argon and then cooled to 85 °C. A solution of the keto enal **7** (77 mg, 0.35 mmol) in DME (12 mL) was perfused into the suspension over a 20-h period by way of a syringe pump, and then the mixture was stirred for a further 12 h before being cooled to rt. The mixture was diluted with anhydrous, deoxygenated hexanes (100 mL) and filtered through a pad of Florisil. The residues were washed with hexanes (150 mL), the combined filtrates were concentrated to a volume of 2 mL by distillation at atmospheric pressure, and then final traces of solvent were removed at 0 °C under reduced pressure. The crude residue (63 mg) was evaporatively distilled at 100 °C/0.07 mmHg to give an oil (31 mg) which by GC analysis (SCOT OV101, 0.5 mm × 40 m, at 175 °C) and GC-MS was shown to contain a mixture of volatile components. There were three major components which in order of elution gave m/z 136, 176 and 190 in a ratio of 0.2:0.2:1. The use of tetradecane as an internal standard indicated that the component m/z 190 had been produced in 15% yield. This component was isolated by preparative GC (vide supra, 175 °C) to give an oil (5 mg, 26 mmol, 8%): ^1H NMR δ 6.25 (dd, J = 17.6, 11.1 Hz, 2 H), 4.98 (dd, J = 11.1, 1.6 Hz) and 4.91 (dd, J = 17.6, 1.6 Hz, 4 H), 2.07 (m, impurity), 1.54 (m, 10 H), 1.26 (m) and 1.09 (m, 6 H); ^{13}C NMR δ 145.99, 111.71, 40.85; 33.40 (br), 31.71 (br), 21.93 (br), 21.56 (br); MS m/z = 190 (7) (M^+), 79 (100); found 190.1730, $C_{14}H_{22}$ requires 190.1721. These spectral characteristics were similar to those reported in the literature[24] for 1,6-divinylbicyclo[4.4.0]decane (**32**).

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Supplementary Material Available: NMR spectra for compounds **12**, **14**, **16**, **17**, **20** and **21**, **22**, **23**, **24**, **7**, **28**, **29**, **30**, and **32** (20 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.