

# Carbocations with Bent Three-Center, Two-Electron C-H-C Bonds

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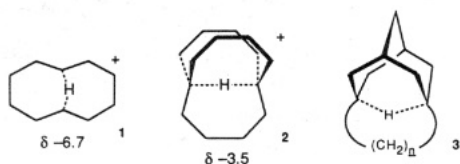
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**Abstract:** We have synthesized a series of carbocations containing bent C-H-C bonds with progressively smaller bond angles (compounds **2**, **4**, **5**, and **6**). As the three-center bond is bent, the chemical shift of the central hydrogen moves strongly upfield while the chemical shift of the bridgehead carbons moves proportionately downfield, indicating that an overall polarization of the bond is occurring. An essentially linear correlation exists between the estimated bond angle and the chemical shift, perhaps due to differences in the vibrational amplitudes of the C-H-C bond.

Though common among inorganic substances, particularly the boron hydrides, three-center, two-electron (3c-2e) bonds<sup>1</sup> are rare in organic chemistry. In fact, the first unequivocal report of an organic substance with a 3c-2e C-H-C bond, the cyclooctyl cation (**1**), did not appear until 1978.<sup>2</sup> Moreover, the first report of a thermally stable substance with a 3c-2e C-H-C bond did not occur until 1984 in our own work on the synthesis and characterization of the *in*-bicyclo[4.4.4]-1-tetradecyl cation (**2**).<sup>3</sup> Characteristic of both cations **1** and **2**, and highly diagnostic of the C-H-C bond, is the presence in the NMR spectrum of an unusual upfield resonance in the range  $\delta$  -3 to -8 due to the bridging hydrogen.

More recently, Sorensen has reported a number of tricyclic cations with the general structure **3** in which the distance between the bridgehead carbons has been systematically varied.<sup>4</sup> He found that as the intrabridgehead distance increased from  $n = 5$  to  $n = 8$ , hydrido bridging became less favorable, until at  $n = 8$  a classical carbocation with no bridging was obtained. This result indicates that the relative orientation of the interacting atoms in space is crucial for promoting the formation of a three-center bond. Theoretical work on the structure of a 3c-2e C-H-C bond in the 2-butyl cation has been published by Schleyer.<sup>5</sup>



Unlike normal two-center covalent bonds, three-center bonds are flexible and can in principle exhibit a continuum of geometries

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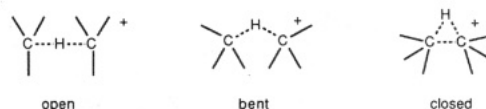
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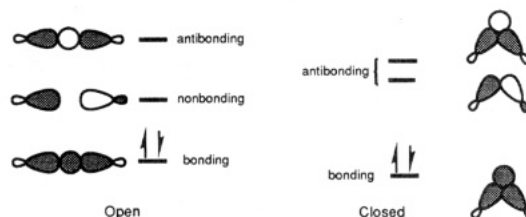
(5) Buzek, P.; Schleyer, P. v. R.; Sieber, S.; Koch, W.; Carneiro, J. W. de M.; Vancik, H.; Sunko, D. E. *J. Chem. Soc. Chem. Commun.* **1991**, 671-674.

ranging from "open" and linear to "closed" and acutely triangular. The open, linear system has no interaction between the terminal atoms, while the closed system has fully developed bonding between all three centers.<sup>6</sup> In between the two extremes lies a continuum of bent structures exhibiting varying degrees of bonding between the terminal atoms.



The geometry of inorganic and organometallic substances with 3c-2e bonds has been studied by both X-ray crystallography and neutron diffraction. The  $B_2H_7^-$  anion, for instance, has a bent B-H-B bond with an angle of  $136^\circ$ ,<sup>7</sup> a value that has been accurately reproduced by a high-level ab initio calculation.<sup>8</sup> An interesting contrast is the structure of the isoelectronic bridged hexamethyldialuminum hydride anion,  $(CH_3)_3Al-H-Al(CH_3)_3$ , which is linear by X-ray crystallography.<sup>9</sup>

The geometries of cations with C-H-C bonds are less well understood. Theoretical studies have indicated that in the absence of steric effects, triangular or bent geometries are preferred to linear ones for 3c-2e bonds.<sup>10</sup> The explanation for this preference is best seen by looking at two MO diagrams, one representing a linear, open system, and the other a closed system. The closed C-H-C bond is more stable than the open one because the fully symmetric bonding combination is lower in energy than its linear counterpart owing to an additional interaction of the carbon atoms.



(6) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176-183.

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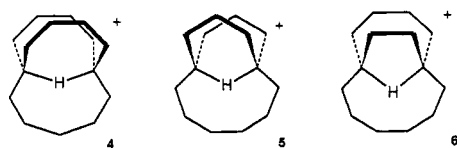
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Having characterized cation **2** with a linear C–H–C bond, we were curious to see what effect bending the three-center bond would have on its properties. The easiest way to do this bending would be to change the size of one or more of the hydrocarbon bridges of the bicyclic framework, thus forcing the three-center bond to adopt a nonlinear geometry. Imbedded in this approach is the assumption that the geometry of the three-center bond is controlled primarily by its steric environment. Calculations have suggested that the stabilization energy derived from the formation of the three-center bond for tertiary carbocationic systems is on the order of only 2–3 kcal/mol,<sup>10</sup> which is probably small in comparison with the energetic effects of skeletal strain in a medium-ring bicyclic molecule.

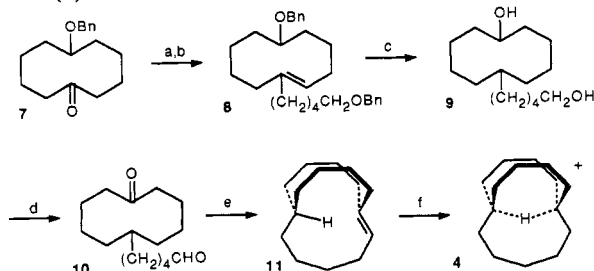
Ideally, we wanted to prepare a set of cations having a range of ring sizes in the bridges and thus having various degrees of C–H–C bending. We expect that the smaller the ring size, the more bent the three-center bond. As suitable targets, we chose the *in*-bicyclo[5.4.4]-1-pentadecyl cation (**4**), the *in*-bicyclo[6.3.3]-1-tetradecyl cation (**5**), and the *in*-bicyclo[6.4.2]-1-tetradecyl cation (**6**).



***in*-Bicyclo[5.4.4]-1-pentadecyl Cation (**4**).** On the assumption that the geometries of various 3c-2e cations are determined primarily by steric considerations, molecular mechanics calculations were carried out to predict a C–H–C bond angle for the *in*-bicyclo[5.4.4]-1-pentadecyl cation (**4**). The central hydrogen was constrained to be equidistant from the two bridgehead carbons, and the experimentally determined bond-stretching force constant of  $1.26 \times 10^5$  dyn/cm was used.<sup>3b</sup> We further assumed that bending force constants would contribute little to the geometry or the length of the three-center bond and thus could be neglected. With these approximations, a value of  $161^\circ$  was predicted for the H–C–H angle in **4**.

The synthesis route to **4** is a modification of our published synthesis of the [4.4.4] cation **2**<sup>3</sup> and is summarized in Scheme I. Reaction of the known<sup>3</sup> benzyloxy ketone **7** with the five-carbon Grignard reagent  $\text{BnO}(\text{CH}_2)_5\text{MgCl}$  in benzene solvent and 1.0 equiv of  $\text{Bu}_4\text{NI}$  gave a tertiary alcohol, which was dehydrated by treatment with  $\text{TsOH}$  in benzene and accompanying azeotropic removal of water to give alkene **8**. Catalytic hydrogenation of **8** over Pd catalyst in ethanol/acetic acid gave diol **9**, and oxidation of **9** with pyridinium chlorochromate provided keto aldehyde **10**. Titanium-induced coupling<sup>11</sup> using our recently optimized conditions<sup>12</sup> then took place in 25% yield to give alkene **11**.

**Scheme I.** Synthesis of *in*-Bicyclo[5.4.4]-1-pentadecyl Cation (**4**)<sup>a</sup>



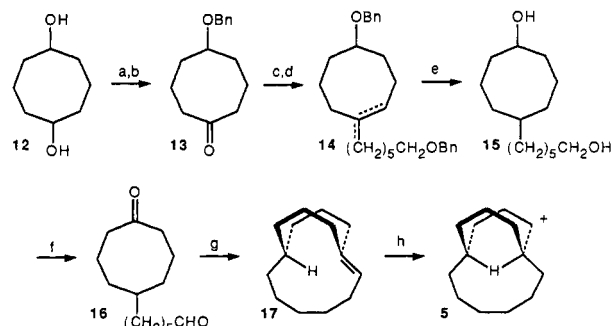
<sup>a</sup> (a)  $\text{BnO}(\text{CH}_2)_5\text{MgCl}$ , benzene,  $\text{Bu}_4\text{NI}$ , 78%; (b)  $\text{TsOH}$ , benzene, reflux, 75%; (c)  $\text{H}_2$ , Pd–C,  $\text{EtOH}/\text{EtOAc}/\text{HOAc}$ , 80%; (d) PCC, NaOAc, 4-Å molecular sieves,  $\text{CH}_2\text{Cl}_2$ , 89%; (e)  $\text{TiCl}_3(\text{DME})_{1.5}$ , Zn–Cu couple, DME, 25%; and (f)  $\text{TiOH}$ ,  $\text{CD}_2\text{Cl}_2$ .

As expected, protonation of alkene **11** with  $\text{TiOH}$  in  $\text{CD}_2\text{Cl}_2$  gave a solution of cation **4**, whose characteristic resonance due to the bridging hydrogen occurred at  $\delta$  –4.5, more than 1 ppm upfield from the analogous resonance in cation **2**. Further, the  $^{13}\text{C}$  chemical shift of the bridgehead carbon appeared at  $\delta$  152.5, some 13.2 ppm downfield from the corresponding [4.4.4] cation bridgehead resonance at  $\delta$  139.3. The IR spectrum of cation **4** as its triflate salt revealed a very wide band of relatively low intensity centered around  $2000\text{ cm}^{-1}$ , consistent with a three-center C–H–C interaction. For comparison, the linear cation **2** has its corresponding IR absorption at  $2113\text{ cm}^{-1}$ .

A variable-temperature  $^{13}\text{C}$  NMR study of cation **4** revealed interesting dynamic behavior. At room temperature, **4** shows six peaks in the NMR spectrum, consistent with average  $\text{C}_{2v}$  symmetry. At  $-30^\circ\text{C}$ , two of the five aliphatic resonances are split cleanly into two sets of two peaks, indicating a molecule in which either the  $\text{C}_2$  axis or the mirror plane ( $\sigma_v$ ) has been conserved. At  $-42^\circ\text{C}$ , the bridgehead carbon peak is split into two resonances of equal intensity at  $\delta$  152.45 and 152.55, although the peaks in the aliphatic region remain sharp and unchanged. Loss of the  $\sigma_v$  plane as a symmetry element requires simultaneous conformational dynamism in all three bridges, whereas loss of the  $\text{C}_2$  axis necessitates conformational mobility only in the five-carbon bridge. We calculated an activation energy of 10.5 kcal/mol for the interconversion process, as determined from NMR line separations and peak coalescence temperatures.

***in*-Bicyclo[6.3.3]-1-tetradecyl Cation (**5**).** Molecular mechanics calculations on the *in*-bicyclo[6.3.3]-1-tetradecyl cation (**5**) suggest that the three-center C–H–C bond should have an angle of approximately  $131^\circ$ , making it considerably more bent than that in cation **4**. As shown in Scheme II, cation **5** was prepared by protonation of the corresponding alkene *in*-bicyclo[6.3.3]-1-tetradecene (**17**). Commercially available 1,5-cyclooctanediol (**12**) was monoprotected by treatment with sodium hydride and benzyl chloride in THF to give the corresponding benzyloxy alcohol, with negligible amounts of the diprotected byproduct. Oxidation of the alcohol with pyridinium chlorochromate then gave ketone **13**, which was treated with a six-carbon benzyloxy-protected Grignard reagent to yield a tertiary alcohol. Dehydration of the alcohol was accomplished by treatment with thionyl chloride in pyridine, and hydrogenation of the double bond and cleavage of the benzyl ethers occurred simultaneously on reduction with  $\text{H}_2$  over a palladium catalyst. The corresponding diol **15** was oxidized to give keto aldehyde **16**, which was then submitted to titanium-induced coupling to give olefin **17**. In *in* geometry of the bridgehead proton in alkene **17** was proven by reducing the product to the corresponding bridgehead alkane, whose  $^{13}\text{C}$  NMR spectrum showed 11 peaks, indicating an alkane with average  $\text{C}_s$  symmetry, as expected for the desired *in,out* isomer.

**Scheme II.** Synthesis of *in*-Bicyclo[6.3.3]-1-tetradecyl Cation (**5**)<sup>a</sup>



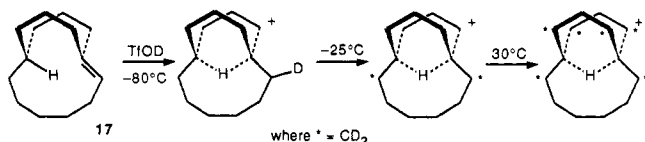
<sup>a</sup> (a) NaH, BnCl,  $\text{Bu}_4\text{NBr}$ , THF, 74%; (b) PCC, NaOAc, 4-Å molecular sieves,  $\text{CH}_2\text{Cl}_2$ , 85%; (c)  $\text{BnO}(\text{CH}_2)_6\text{MgCl}$ , benzene,  $\text{Bu}_4\text{NI}$ , 75%; (d)  $\text{SOCl}_2$ , pyridine, 75%; (e)  $\text{H}_2$ , Pd–C,  $\text{EtOH}/\text{EtOAc}/\text{HOAc}$ , 80%; (f) PCC, NaOAc, 4-Å molecular sieves,  $\text{CH}_2\text{Cl}_2$ , 95%; (g)  $\text{TiCl}_3(\text{DME})_{1.5}$ , Zn–Cu couple, DME, 30%; and (h)  $\text{TiOH}$ ,  $\text{CD}_2\text{Cl}_2$ .

Treatment of alkene **17** with an excess of triflic acid (TfOH) in  $\text{CD}_2\text{Cl}_2$  at room temperature under argon gave a clean, light yellow solution of cation **5**. The bridging proton appeared at  $\delta$  -6.42, more than 3 ppm upfield from the corresponding resonance in the [4.4.4] cation **2** and consistent with the result for the [5.4.4] cation **4**. In the  $^{13}\text{C}$  NMR spectrum of **5**, the peak attributable to the bridgehead carbons is at  $\delta$  178.8, some 39.5 ppm downfield from that for cation **2** ( $\delta$  139.3).

The  $^{13}\text{C}$  spectrum of **5** shares some dynamic features with that of cation **4**. At room temperature, the spectrum has eight peaks, indicating a molecule with an average  $\text{C}_2$  axis or a plane of symmetry lying midway between the bridgehead carbons. The peaks begin to show line broadening at  $-45^\circ\text{C}$ , and at  $-80^\circ\text{C}$ , the spectrum has 14 peaks, indicating a complete lack of symmetry. Also at  $-80^\circ\text{C}$ , the bridgehead peak is split into two resonances of equal intensity at  $\delta$  178.2 and 178.0. An activation energy of 9.78 kcal/mol for the symmetrization process was calculated from the coalescence temperature and the terminal line-separation values.

The [6.3.3] alkene **17** proved to require stronger acids to effect protonation than did the [4.4.4] cation **2**. Trifluoroacetic acid produced only partial protonation, and triflic acid was required to completely protonate the alkene. Several other acids, including fluorosulfonic acid and HCl in  $\text{CD}_2\text{Cl}_2$ , were also used to effect protonation, but the chemical shifts of the resultant cation proved to be essentially invariant over a number of different acidic media.

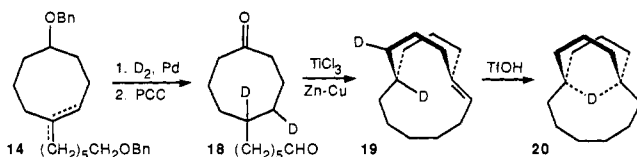
Cation **5** exhibits some interesting protonation/deprotonation behaviors at low temperatures. For instance, treatment of alkene **17** with deuterated triflic acid (TfOD) in  $\text{CF}_3\text{COOD}$  and  $\text{CD}_2\text{Cl}_2$  at  $30^\circ\text{C}$  results in the complete exchange of hydrogens vicinal to the bridgehead. (The bridgehead hydrogen is not exchanged under any circumstances.) At  $-25^\circ\text{C}$ , however, only four hydrogen atoms are exchanged for deuterium, resulting in the collapse of the broad singlet at 2.5 ppm in the  $^1\text{H}$  NMR spectrum. We believe that at this lower temperature, deuterium exchange is confined to the more flexible six-carbon bridge, since molecular mechanics calculations indicate that the intermediate alkene **17** with the double bond in the larger bridge is less strained by 4 kcal than the positional isomer with the double bond in the three-carbon bridge.



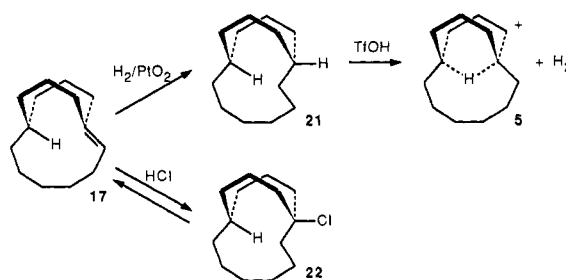
Only one deuterium atom is incorporated into alkene **17** on treatment with TfOD in  $\text{CH}_2\text{Cl}_2$  at  $-80^\circ\text{C}$ , a fact we used to our advantage for performing an isotope-perturbation NMR experiment on cation **5**.<sup>13</sup> The bridgehead resonance in the  $^{13}\text{C}$  NMR spectrum of monodeuterated **5** was split by 2.8 ppm, consistent with a nonclassical ion. In addition, the IR spectrum of **5** revealed a broad absorption at  $1750\text{ cm}^{-1}$ , which collapsed when a bridging deuterium atom was substituted for the bridging hydrogen (**20**). This band agrees well with the value found by Schleyer for the cyclooctyl cation ( $1845\text{ cm}^{-1}$ ).<sup>14</sup> Unfortunately, no new peaks ascribable to C-D stretching could be detected, probably because isotopic substitution had shifted the vibration to a part of the spectrum occupied by other strong absorptions. Several points about the IR spectrum of **5** are worth noting. The C-H-C

absorption is much broader in **5** than it is in **2** and is red-shifted by  $263\text{ cm}^{-1}$ . This result is consistent with a bent three-center bond, in which lower-energy bending vibrations have combined with the pure asymmetric stretch.

The synthesis of the labeled *in*-deuterio cation **20** was accomplished in a straightforward manner by reduction of **14** with  $\text{D}_2$  gas in a mixture of EtOD and  $\text{CD}_3\text{COOD}$ . Oxidation gave keto aldehyde **18**, titanium-induced coupling gave **19**, and protonation with triflic acid at  $30^\circ\text{C}$  washed out the extraneous deuterium atom on the bridge, giving cation **20**.

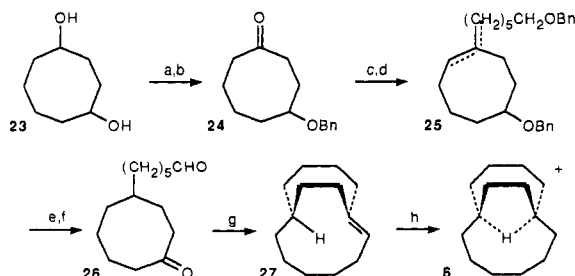


One further interesting reaction in the [6.3.3] system is that the bicycloalkane **21**, prepared by hydrogenation of alkene **17** over  $\text{PtO}_2$  in ethanol, undergoes a smooth protonolysis on reaction with triflic acid in dichloromethane at room temperature to yield a clean solution of cation **5**. The reaction is similar to the previously studied protonolysis of *in,out*-bicyclo[4.4.4]tetradecane.<sup>5</sup> In addition, treatment of alkene **17** with dry HCl gas in chloroform results in the formation of bridgehead chloride **22**, which spontaneously loses HCl gas to regenerate **17** on exposure to the atmosphere. The reaction is considerably slower at low temperatures and could be monitored by NMR by placing a needle outlet at the top of the NMR tube to permit the loss of HCl gas. At  $0^\circ\text{C}$  in  $\text{CHCl}_3$  solution, the half-life of the bridgehead chloride **22** is approximately 5 min, making it among the most solvolitically reactive tertiary halides known to date.<sup>4</sup>



***in*-Bicyclo[6.4.2]-1-tetradecyl Cation (6).** Molecular mechanics calculations indicate that the *in*-bicyclo[6.4.2]-1-tetradecyl cation (**6**) should have the most bent bond of all the cations studied, with a C-H-C angle of  $113^\circ$ . The synthesis of the precursor alkene **27** is conceptually similar to that of the other alkene precursors and is shown in Scheme III. Commercially available 1,4-cyclooctanediol (**23**) was monoprotected by treatment with NaH

**Scheme III.** Synthesis of *in*-Bicyclo[6.4.2]-1-tetradecyl Cation (**6**)<sup>a</sup>



<sup>a</sup> (a) NaH, BnCl,  $\text{Bu}_4\text{NBr}$ , THF, 67%; (b) PCC, NaOAc, 4-Å molecular sieves,  $\text{CH}_2\text{Cl}_2$ , 90%; (c)  $\text{BnO}(\text{CH}_2)_6\text{MgCl}$ , benzene,  $\text{Bu}_4\text{NI}$ , 65%; (d) TsOH, benzene, reflux, 70%; (e)  $\text{H}_2$ , Pd-C, EtOH/EtOAc/HOAc, 77%; (f) PCC, NaOAc, 4-Å molecular sieves,  $\text{CH}_2\text{Cl}_2$ , 78%; (g)  $\text{TiCl}_3(\text{DME})_{1.5}$ , Zn-Cu couple, DME, 36%; and (h) TfOH,  $\text{CD}_2\text{Cl}_2$ .

(11) For reviews of the titanium-induced coupling reaction, see: (a) McMurtry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405-411. (b) McMurtry, J. E. *Chem. Rev.* **1989**, *89*, 1513-1524. (c) Lenoir, D. *Synthesis* **1989**, 833-897.

(12) McMurtry, J. E.; Lectka, T.; Rico, J. G. *J. Org. Chem.* **1989**, *54*, 3748-3749.

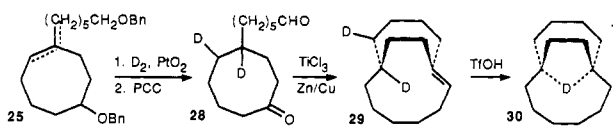
(13) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070-8071.

(14) Buzek, P.; Schleyer, P. v. R.; Vancik, H.; Sunko, D. E. *J. Chem. Soc. Chem. Commun.* **1991**, 1538-1540.

and benzyl chloride in refluxing THF, and the resulting benzyloxy alcohol was oxidized to ketone **24** by reaction with PCC in  $\text{CH}_2\text{Cl}_2$  in the presence of powdered molecular sieves and sodium carbonate. Reaction of the appropriate six-carbon Grignard reagent with ketone **24** in benzene produced the corresponding tertiary alcohol in 65% yield, and dehydration with thionyl chloride in pyridine gave alkene **25**. Simultaneous reduction of the double bond and cleavage of the benzyl ether groups were achieved by catalytic hydrogenation over Pd-C in EtOH/HOAc. Oxidation of the intermediate diol with PCC yielded keto aldehyde **26**, which was immediately coupled to the bicyclic alkene **27** in 30% yield.

Alkene **27** can be protonated by TfOH at  $-20^\circ\text{C}$  to form a stable solution of cation **6**, which decomposes slowly on warming to room temperature. The characteristic resonance due to the bridging proton appears at  $\delta -6.5$ , making it the most shielded of any bridging hydrogen in a ditertiary C-H-C cation known to date. The  $^{13}\text{C}$  NMR spectrum of **6** has six peaks at  $-70^\circ\text{C}$ , indicative of a species with average  $C_3$  symmetry. As the temperature is raised, selective line broadening and coalescence of peaks gradually set in, until only two broad lines are discernable in the spectrum at  $10^\circ\text{C}$ .

The IR spectrum of the [6.4.2] cation **6** was measured in  $\text{CH}_2\text{Cl}_2$  solution at  $-20^\circ\text{C}$ . A broad band centered at about  $1720\text{ cm}^{-1}$  collapsed on isotopic substitution of the bridging hydrogen as in the case of the [6.3.3] cation. Again, this is consistent with a weakened and/or bent C-H-C interaction. The synthesis of the *in*-deuterio cation **30** was accomplished by reduction of alkene **25** with  $\text{D}_2$  gas in MeOD/DOAc solvent followed by oxidation, carbonyl coupling, and treatment with triflic acid.



**Molecular Orbital Calculations.** Molecular orbital calculations were performed on cations **2**, **4**, **5**, and **6** using both semiempirical and ab initio methods. For cation **2**, AM1 calculations predict an overall  $D_3$  symmetry, a linear, centrosymmetric C-H-C bond, a C-H bridgehead distance of 131 pm, and a heat of formation of 129.55 kcal/mol. The bridgehead carbons each carry a calculated charge of +0.154, while the bridging hydrogen carries only a +0.019 charge.

In order to estimate the amount of stabilization due to the formation of the three-center bond, cation **2** was optimized at the AM1 level with the bridgehead C-H bond constrained to be 112 pm, a typical distance for a tertiary C-H bond. In this case, the cation is essentially restricted to a classical geometry. The calculated heat of formation is 131.46 kcal/mol, suggesting a stabilization energy of approximately 2 kcal/mol for the non-classical ion. From prior experience, we expect this value to define a lower limit on the expected stabilization energy, owing to the well-documented tendency of semiempirical methods such as AM1 to underestimate the energies of nonclassical cations.<sup>2</sup> MNDO, PM3, and MINDO/3 semiempirical methods predicted essentially the same result.

Cation **2** was also optimized at the 3-21G ab initio level, with imposed  $C_3$  symmetry to simplify the calculational problem. The ab initio result indicated a symmetric C-H-C bond but with a C-H distance of 122 pm, about 10 pm shorter than that predicted by AM1 and indicative of a stronger three-center interaction. When the lower-level STO-3G basis set was employed, a slightly longer, although still symmetric, C-H interaction of 125 pm resulted. The trend seems to be that as more sophisticated computational levels are employed on the [4.4.4] cation, the three-center interaction appears stronger.

AM1 calculations on the [5.4.4] cation **4** predict a largely classical structure ( $\Delta H_f = 129.11\text{ kcal/mol}$ ) with a weak, unsymmetric C-H-C interaction. The structure is characterized

by an elongated bridgehead C-H bond of 118 pm, with the opposite bridgehead, which carries most of the positive charge, 168 pm away. Full optimization of the [6.3.3] cation **5** gave similar results, predicting a classical ion with a slightly elongated C-H bridgehead bond of 121 pm and  $\Delta H_f = 132.62\text{ kcal/mol}$ .

The [6.3.3] cation **5** was also optimized at the AM1 level with the constraint that both C-H lengths of the three-center bond be equal. In this case, a structure of negligibly higher energy results ( $\Delta H_f = 132.94\text{ kcal/mol}$ ) with C-H bond lengths of 134 pm. The constrained structure is nevertheless not a minimum on the potential energy surface, as was indicated by a vibrational analysis. A fully optimized 3-21G calculation of **5** could not be undertaken for financial reasons, but an optimization with imposed  $C_2$  symmetry yielded a C-H bond length of 128 pm.

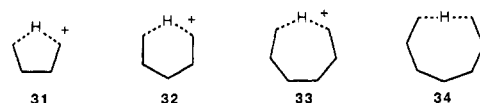
AM1 optimization of the [6.4.2] cation **6** yielded a classical structure, with a small polarization of the C-H bond by the carbocationic center at the other bridgehead. The C-H bond length in this classical species is 113.4 pm, the opposite bridgehead is 206.7 pm away, and  $\Delta H_f = 134.20\text{ kcal/mol}$ . When the two C-H distances were constrained to the same value, a bond length of 136.6 pm resulted with  $\Delta H_f = 140.55\text{ kcal/mol}$ . The atomic charges for the symmetrically constrained structure were +0.148 for the bridgehead carbons and +0.043 for the bridging hydrogen. Once again, the use of alternative MNDO and PM3 methodologies gave basically the same result. A summary of AM1 computational results for cations **2**, **4**, **5**, and **6** is given in Table I.

Table I. AM1 Data for Bicyclic Cations

cation	bond angle (degrees)	$\nu\text{ (cm}^{-1}\text{)}$		C-H length (pm)	charge	
		exptl	calc		on C	on H
<b>2</b>	180.0	2130	1854	131	+0.154	+0.019
<b>4</b>	166.2	2000	1727	133	+0.155	+0.020
<b>5</b>	134.7	1800	1881	134	+0.128	+0.055
<b>6</b>	113.6	1750	1753	137	+0.148	+0.043

Two conclusions can be drawn from the computational results. First, the semiempirical method seems to underestimate the contributions of C-H-C interaction. Second, there is no simple relationship between the Mulliken-derived charge and the chemical shift of the bridging hydrogen. Frequency calculations using the AM1 basis are compared in Table I to the experimental IR vibrations. In the case of cation **2**, the optimization was unconstrained. For the remaining three cations, the C-H-C bonds were constrained to be centrosymmetric.

In order to obtain a rough idea of the changes that could be expected on bending of the three-center bonds in computationally simpler systems, fully optimized molecular orbital calculations were performed on the monocyclic cations **31-34** at the 3-21G ab initio level. In all cases, the 3c-2e species proved to be at least local minima on the potential energy surface, a fact confirmed by vibrational analyses which resulted in only real frequencies. Cation **31** optimized to approximate  $C_2$  symmetry, whereas cation **32** converged to approximate  $C_s$  symmetry, cation **33** to  $C_2$  symmetry, and cation **34** to  $C_s$ . Cation **31** bears a structural resemblance to the [6.4.2] cation **6** in that both have geometry-defining five-membered rings. Similarly, cations **32** and **5** are related, as are **2** and **33**, and **4** and **34**.



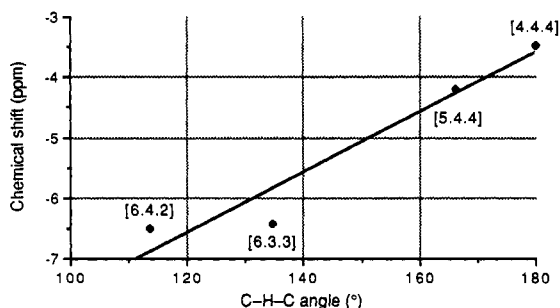
Several interesting trends appear in the calculations for **31-34**. For instance, as the size of the ring increases, the C-H-C bond angle tends toward  $180^\circ$ . The length of the C-H interaction also decreases, which suggests that the bent cations have longer and hence more polarized three-center bonds. Once again, no clear correlation can be made between the atomic charge and the

**Table II.** 3-21G Data for Monocyclic Cations 31–33

cation	bond angle (degrees)	$\nu$ (cm <sup>-1</sup> )	charge on H	C-H distance (pm)
31	120.4	1987	+0.038	130
32	144.9	2218	+0.032	126
33	171.2	2490	-0.036	123

chemical shifts of the hydrido bridge; in fact, the trend seems to be in the opposite direction to that of experiment. As has been pointed out, however, no simple correlation between the atomic charge and the chemical shift is to be expected.<sup>14,15</sup> Values for the frequencies of the IR active asymmetric stretch were also determined for the monocyclic cations, consistent with a trend toward longer and weaker C-H-C bonds in the smaller bridged cations. This result suggests that a similar pattern should hold for bicyclic cations **2**, **5**, and **6**. Table II summarizes the ab initio results for the monocyclic cations.

One of the most intriguing results uncovered in this study is the observation that the chemical shift of the bridging hydrogen moves to higher fields as the C-H-C angle increases. As can be seen from a plot of AM1 C-H-C bond angle versus chemical shift (Figure 1), the correlation is fairly good. The reasons for this correlation are not obvious, but one attractive suggestion made recently by Cioslowski<sup>16</sup> has to do with the changes in the vibrational amplitude that accompany bending in the C-H-C bond. Ab initio calculations on the linear cation **2** at the HF/6-311G\*\* level predict a charge on the bridging hydrogen of -0.228, and chemical shift calculations using the GIAO-CPHF approach<sup>17</sup> predict a shift for the bridging hydrogen of  $\delta$  -10.06, some 6.6 ppm *higher* field than the experimental value ( $\delta$  -3.46). It has been suggested<sup>16</sup> that the discrepancy is due to the relatively large vibrational motions of the bridging hydrogen. The experimental shift is a vibrationally averaged value, whereas the calculated shift is a frozen-nuclei value. If this argument is correct and the frozen-nuclei shift for all of the 3c-2e cations is near  $\delta$  -10, then the upfield shift on bending the C-H-C bond might be due to more restricted vibrational motions. In other words, the greater the C-H-C angle, the smaller the vibrational motion and the closer the chemical shift is to the "expected"  $\delta$  -10. The variation of the C-H-C asymmetric stretch frequency with the bond angle, both calculated and experimental, is consistent with this explanation (Tables I and II).

**Figure 1.** Correlation of C-H-C bond angle (AM1) versus chemical shift.

## Conclusion

In summary, we have synthesized a series of carbocations containing bent C-H-C bonds with progressively smaller bond angles. As the three-center bond is bent, the chemical shift of the central hydrogen moves strongly upfield while the chemical shift of the bridgehead carbons moves proportionately downfield,

indicating that an overall polarization of the bond is occurring. An essentially linear correlation exists between the estimated bond angle and the chemical shift, perhaps due to differences in the vibrational amplitudes of the C-H-C bond.

## Experimental Section

**General.** Melting points were recorded on a Thomas-Hoover apparatus. UV spectra were recorded on a Perkin-Elmer Model 552A instrument, IR spectra were recorded on either a Perkin-Elmer Model 298 or a Polaris Fourier Transform instrument and NMR spectra were recorded on Varian VXR-200 (200 MHz) or Varian VXR-400 (400 MHz for <sup>1</sup>H NMR and 80 MHz for <sup>13</sup>C NMR) instruments. All reactions were conducted under an atmosphere of argon unless otherwise noted. All solvents were distilled prior to use. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were doubly distilled from potassium metal. Dichloromethane was distilled from CaH<sub>2</sub>. Anhydrous diethyl ether was obtained from Mallinckrodt and used without further purification.

**1-(5-Benzoyloxy)pentyl-6-(benzyloxy)-1-cyclodecene (8).** A Grignard reagent prepared from 5-(benzyloxy)-1-chloropentane (20 g, 94 mmol) and Mg turnings (4.0 g, 16.6 mmol) in 200 mL of dry ether was concentrated by removal of the solvent at high vacuum to afford a thick paste. Benzene (150 mL) and Bu<sub>4</sub>NBr (5.0 g) were added to the paste with stirring, and the resulting solution was cooled in an ice-salt bath to -10 °C. 6-(Benzyloxy)cyclodecanone (**7**) (21.1 g, 80 mmol) in 100 mL of benzene was added dropwise over 10 min, and the green-gray solution was allowed to warm to room temperature (1 h). The reaction mixture was then diluted with ether and washed with saturated aqueous NH<sub>4</sub>Cl (100 mL) and water (100 mL). Drying (MgSO<sub>4</sub>) and concentration followed by chromatography on silica gel (1:3 ether/hexane) yielded 28.8 g (62.4 mmol, 78%) of tertiary alcohol as a mixture of diastereomers: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  7.4–7.2 (m, 10 H), 4.5–4.4 (s, 4 H), 3.7–3.3 (m, 3 H), 2.0–1.1 (m, 24 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 80 MHz)  $\delta$  139.0, 128.4, 128.3, 128.2, 128.1, 127.9, 127.4, 79.3, 78.2, 75.2, 74.9, 73.3, 71.2, 70.9, 70.5, 44.7, 43.7, 37.2, 37.0, 34.9, 34.6, 34.0, 30.4, 30.2, 26.6, 23.2, 23.1, 22.3, 21.5, 18.9; IR (CHCl<sub>3</sub>) 3600 cm<sup>-1</sup>.

The tertiary alcohol (20 g, 43 mmol), TsOH (0.5 g), and benzene (400 mL) were refluxed for 5 h with accompanying azeotropic removal of water. The solution was then cooled, diluted with ether (250 mL), washed with saturated NaHCO<sub>3</sub> (2 × 100 mL) and water (100 mL), and dried (MgSO<sub>4</sub>). The residue was purified by chromatography on silica gel (5% ether/hexane) to yield alkene **8** as a clear yellow liquid (13.2 g, 31.4 mmol, 75%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  7.4–7.2 (m, 10 H), 5.4–5.2 (m, 1 H), 4.5–4.4 (s, 4 H), 3.7–3.3 (m, 3 H), 2.0–1.1 (m, 23 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 80 MHz)  $\delta$  141.2, 139.6, 139.0, 128.8, 128.7, 128.0, 127.9, 127.6, 123.3, 80.5, 73.1, 70.9, 70.7, 38.0, 36.6, 34.5, 32.3, 31.1, 30.3, 30.1, 29.8, 29.1, 27.2, 26.4, 25.5, 23.8, 18.9; FT-IR (CHCl<sub>3</sub>) 1655 cm<sup>-1</sup>.

**6-(5-Hydroxypentyl)-1-cyclodecanol (9).** A solution of alkene **8** (5.2 g, 12.4 mmol) in 30 mL of 20:2:1 MeOH/EtOAc/HOAc containing 1 g of 10% Pd-C was hydrogenated in a Parr apparatus at 50 psi for 48 h. The mixture was then filtered, diluted with ether, washed with saturated aqueous NaHCO<sub>3</sub> (50 mL), dried (MgSO<sub>4</sub>), and concentrated. The resulting oil was purified by chromatography on silica gel (1:1 ether/hexane) to yield a clear oil as a 1:1 mixture of diastereomers (2.39 g, 9.9 mmol, 80%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  4.0 (m, 1 H), 3.9 (m, 1 H), 3.7 (m, 3 H), 1.9–1.1 (m, 25 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 80 MHz)  $\delta$  72.8, 71.6, 61.5, 35.7, 35.0, 34.5, 33.9, 33.5, 32.2, 30.8, 26.9, 25.2, 22.4, 21.9; IR (neat) 3430 cm<sup>-1</sup>.

**6-(Oxopentyl)-1-cyclodecanone (10).** Diol **9** (2.0 g, 8.2 mmol) in 10 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was added dropwise with stirring at 0 °C to a mixture containing CH<sub>2</sub>Cl<sub>2</sub> (100 mL), pyridinium chlorochromate (PCC, 3.9 g, 18 mmol), NaOAc (0.5 g), and powdered molecular sieves (1.0 g). The brown suspension was stirred for 2 h and then diluted with ether (50 mL). Filtration through Florisil and concentration yielded keto aldehyde **10** as a clear oil (1.89 g, 89%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  9.77 (t, 1 H), 2.7–2.2 (m, 6 H), 2.0–0.8 (m, 19 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 80 MHz)  $\delta$  215.1, 202.7, 44.4, 42.1, 35.4, 29.9, 23.4, 23.3, 19.5, 18.8; IR (neat) 1710, 1690 cm<sup>-1</sup>.

**in-Bicyclo[5.4.4]-1-pentadecene (11).** A slurry of titanium coupling reagent<sup>12</sup> was prepared by refluxing 10 g of TiCl<sub>3</sub>(DME)<sub>1.5</sub> complex, 5 g of Zn-Cu couple, and 300 mL of DME for 3 h. Keto aldehyde **10** (250 mg, 1.05 mmol) in 50 mL of DME was added to the reaction flask by syringe pump over the course of 35 h. The mixture was then cooled to room temperature and diluted with distilled, degassed pentane (300 mL) and filtered through Florisil under argon. The solvent was distilled off

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(16) Cioslowski, J. *J. Am. Chem. Soc.* **1993**, *115*, 5177–5178.

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at atmospheric pressure, and the residue was purified by preparative GC (OV-101 on Supelcoport at 170 °C) to yield 48 mg (22%) of alkene **11** as a clear oil:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  5.6 (dd, 1 H), 2.95 (m, 1 H), 2.6–0.7 (m, 24 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  143.0, 131.6, 36.8, 35.9, 35.0, 33.7, 33.5, 32.2, 31.8, 29.6, 28.8, 27.4, 26.4, 25.7, 23.0, 22.6; MS (CI)  $m/e$  206 ( $\text{M}^+$ ).

**in-Bicyclo[5.4.4]-1-pentadecyl Cation (4).** Alkene **11** (2.0 mg, 0.01 mmol) was dissolved in  $\text{CD}_2\text{Cl}_2$  (0.5 mL) in a flame-dried NMR tube under argon, and TFOH (5.0 mg, 0.033 mmol) was added to the solution through a syringe at 0 °C. The tube was capped and shaken to yield an orange solution of cation **4**, which proved to be stable for several days at room temperature:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 22 °C)  $\delta$  2.5 (br s, 14 H), 1.9 (br s, 12 H), –4.20 (br s, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 80 MHz, 0 °C)  $\delta$  152.50, 44.6, 42.9, 31.5, 25.8, 21.4; FT-IR ( $\text{CH}_2\text{Cl}_2$ ) 2000  $\text{cm}^{-1}$ .

**5-(Benzyloxy)-1-cyclooctanone (13).** *cis*-1,5-Cyclooctanediol (100 g, 0.69 mmol) was stirred at reflux with NaH (16.6 g, 0.69 mol),  $\text{Bu}_4\text{NBr}$  (10.0 g, 0.03 mol), and benzyl chloride (87.5 g, 0.69 mol) in 500 mL of THF for 8 h. The resulting brown mixture was diluted with 500 mL of diethyl ether and was washed with water (300 mL). The ether solution was dried over  $\text{MgSO}_4$  and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (4:1 ether/hexane) to yield the benzyloxy alcohol as a clear, colorless oil (120 g, 0.51 mol, 74%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  7.37–7.30 (m, 5 H), 4.49 (s, 2 H), 3.81–3.72 (m, 1 H), 3.49–3.43 (m, 1 H), 2.49–2.46 (s, 1 H), 1.96–1.85 (m, 6 H), 1.73–1.38 (m, 6 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  138.4, 127.8, 127.0, 126.9, 78.2, 71.2, 69.6, 36.0, 32.3, 20.2; IR ( $\text{CHCl}_3$ ) 3600  $\text{cm}^{-1}$ .

The benzyl-protected alcohol from the previous step (50 g, 213 mmol) was stirred with pyridinium chlorochromate (PCC, 70 g, 314 mmol), powdered molecular sieves (30 g), and  $\text{Na}_2\text{CO}_3$  (20 g) in 200 mL of  $\text{CH}_2\text{Cl}_2$  at 0 °C until TLC indicated disappearance of starting material (usually 1 h). The reaction mixture was then diluted with an equal volume of ether and filtered through Florisil. Concentration of the filtered solution on a rotary evaporator yielded pure ketone **13** as a clear oil (45 g, 0.193 mol, 90%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  7.42–7.28 (m, 5 H), 4.44 (s, 2 H), 3.33–3.24 (m, 1 H), 2.64–2.54 (m, 2 H), 2.35–2.18 (m, 2 H), 2.14–2.05 (m, 2 H), 1.97–1.89 (m, 2 H), 1.85–1.71 (m, 4 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  216.2, 138.4, 128.2, 127.4, 127.3, 77.9, 70.6, 42.3, 33.8, 23.0; IR (neat) 1693  $\text{cm}^{-1}$ .

**1-(6-(Benzyloxy)hexyl)-5-(benzyloxy)-1-cyclooctene (14).** A Grignard reagent prepared from 1-(benzyloxy)-6-chlorohexane (40 g, 190 mmol), Mg turnings (4.6 g, 190 mmol), and dry ether (150 mL) was concentrated by high vacuum to a thick paste, diluted with benzene (150 mL), and cooled in an ice-salt bath. Benzyloxy ketone **13** (37.1 g, 160 mmol) was added at once to the stirred solution. After 10 min, the reaction mixture was diluted with ether (150 mL) and washed with 1 N HCl (100 mL), dried ( $\text{MgSO}_4$ ), and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel (6:1 ether/hexane as eluent) to afford the tertiary alcohol as a clear, colorless oil (58.5 g, 140 mmol, 60%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  7.4–7.2 (m, 10 H), 4.5–4.4 (s, 4 H), 3.7–3.3 (m, 3 H), 2.0–1.1 (m, 24 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  139.1, 128.8, 128.1, 128.0, 127.95, 127.9, 127.8, 79.6, 78.2, 75.2, 74.9, 73.3, 70.9, 70.7, 70.6, 43.7, 42.7, 37.4, 37.2, 35.1, 34.6, 34.2, 30.6, 30.2, 26.7, 23.6, 23.4, 23.3, 20.5, 19.6; IR ( $\text{CHCl}_3$ ) 3600  $\text{cm}^{-1}$ .

Thionyl chloride (16.7 g, 140 mmol) was added dropwise to a stirred solution of the tertiary alcohol from the previous step (58.5 g, 140 mmol), pyridine (22 mL, 280 mmol), and  $\text{CH}_2\text{Cl}_2$  (200 mL) at 0 °C. After 20 min, the reaction mixture was diluted with pentane, washed with water (100 mL), and dried over  $\text{MgSO}_4$ . Concentration of the solution by rotary evaporation was followed by column chromatography of the crude product on silica gel (3% ether in hexane) to yield the benzyloxy-protected alkene **14** as a clear, colorless oil (48.2 g, 120 mmol, 85%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  7.4–7.2 (m, 10 H), 5.4–5.2 (m, 1 H), 4.5–4.4 (s, 4 H), 3.7–3.3 (m, 3 H), 2.0–1.1 (m, 23 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  141.0, 139.6, 139.2, 128.82, 128.78, 128.1, 128.0, 127.8, 123.7, 80.8, 73.3, 71.0, 70.7, 38.2, 35.7, 34.3, 32.1, 30.2, 29.9, 29.85, 29.6, 28.4, 26.6, 25.9, 23.8, 19.7; FT-IR ( $\text{CHCl}_3$ ) 1660  $\text{cm}^{-1}$ .

**5-(6-Hydroxyhexyl)-1-cyclooctanol (15).** Alkene **14** (20 g, 50 mmol) in a solution of 10:1 ethanol/acetic acid (50 mL) was hydrogenated at 50 psi over Pd–C for 24 h at room temperature. The mixture was then diluted with ether, filtered, and concentrated by rotary evaporation. Chromatography of the crude product on silica gel (diethyl ether as eluent) afforded pure diol **15** as a transparent gum (10 g, 87%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  4.1 (m, 1 H), 3.9 (m, 1 H), 3.7 (m, 3 H), 1.9–1.1 (m, 23

H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  72.65, 72.6, 63.5, 36.9, 35.2, 34.1, 33.9, 33.2, 30.2, 27.7, 26.2, 23.4, 22.0; IR (neat) 3440  $\text{cm}^{-1}$ .

**5-(6-Oxoheptyl)-1-cyclooctanone (16).** Diol **15** (1.0 g, 4.4 mmol) in 80 mL of dry  $\text{CH}_2\text{Cl}_2$  was added dropwise with stirring at 0 °C to a mixture containing  $\text{CH}_2\text{Cl}_2$  (100 mL), pyridinium chlorochromate (3.5 g, 16.2 mmol), NaOAc (1.0 g), and powdered molecular sieves (1.0 g). The resulting brown suspension was stirred for 2 h and diluted with ether (100 mL). Filtration through Florisil and concentration yielded keto aldehyde **16** as a clear oil (950 mg, 95%), which was used immediately in the next step:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  9.8 (s, 1 H), 2.7–2.0 (m, 6 H), 1.8–1.0 (m, 17 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  218.0, 43.9, 42.4, 38.9, 36.2, 34.0, 29.3, 26.8, 25.3, 22.0; FT-IR ( $\text{CHCl}_3$ ) 1710, 1690  $\text{cm}^{-1}$ .

**in-Bicyclo[6.3.3]-1-tetradecene (17).**  $\text{TiCl}_3(\text{DME})_{1.5}$  (7.0 g, 20.9 mmol) and Zn–Cu couple (4.0 g, 61.9 mmol) were added to 280 mL of DME in a 500-mL two-necked flask through a Schlenk tube under argon. The mixture was stirred vigorously at reflux for 3 h to yield a green-black to black homogeneous slurry. Keto aldehyde **21** (50 mg, 0.223 mmol) in 50 mL of DME was added to the stirred mixture through a syringe pump over 35 h. The mixture was then cooled to room temperature and diluted with distilled, degassed pentane (300 mL) and filtered through Florisil under argon. The solvent was distilled off at atmospheric pressure, and the residue was purified by preparative GC (OV-101 on Supelcoport at 170 °C) to yield 15 mg of olefin **17** (35%) as a waxy, white solid:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  5.4 (s, 1 H), 5.1–5.0 (dd, 1 H), 3.3–3.2 (m, 1 H), 2.6–0.7 (m, 22 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  148.4, 141.8, 124.6, 120.8, 42.5, 39.4, 38.0, 35.5, 35.4, 34.6, 34.2, 33.5, 32.5, 31.4, 30.8, 29.7, 28.3, 28.0, 27.4, 26.1, 25.9, 25.5, 25.2, 25.0, 23.4, 21.8; MS (CI)  $m/e$  192 ( $\text{M}^+$ ).

**in-Bicyclo[6.3.3]-1-tetradecyl Cation (5).** Alkene **17** (2.0 mg, 0.01 mmol) was dissolved in  $\text{CD}_2\text{Cl}_2$  (0.5 mL) in a dry NMR tube under argon, and trifluoromethanesulfonic acid (5.0 mg, 0.033 mmol) was added to the solution through a syringe at 0 °C. The tube was then capped and shaken to afford a yellow solution of cation **5** which proved to be stable over a period of days at room temperature:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 200 MHz)  $\delta$  2.8–2.6 (m, 6 H), 2.4–2.2 (m, 6 H), 1.8 (m, 4 H), 1.6–1.4 (m, 4 H), 1.6 (s, 4 H), –6.4 (m, 1 H);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 80 MHz, 25 °C)  $\delta$  178.2, 44.3, 40.5, 38.5, 24.8, 22.8; FT-IR ( $\text{CH}_2\text{Cl}_2$ , trifluoromethanesulfonate salt) 1800  $\text{cm}^{-1}$  (br).

**in,out-Bicyclo[6.3.3]tetradecene (21).** *in*-Bicyclo[6.3.3]-1-tetradecene (**17**; 10 mg, 0.1 mmol), platinum(IV) oxide (10 mg, 0.044 mmol), and 1 mL of MeOH were hydrogenated (50 psi) in a Parr apparatus for 24 h. The mixture was diluted with 1:1 ether/pentane (5 mL) and filtered through a small amount of silica gel. The bulk of the solvent was removed by rotary evaporation (caution: product is highly volatile) followed by high vacuum for 15 s. The crude oil was purified by preparative GC (10% SP 1000 on 80/100 Supelcoport at 170 °C) to yield 7 mg of **21** (70%) as a clear, colorless oil:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  2.5–2.4 (m, 1 H), 1.7–1.0 (m, 23 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  39.8, 34.2, 30.0, 29.4, 29.2, 28.1, 25.9, 25.8, 25.5, 24.2, 23.8; MS (CI)  $m/e$  194 ( $\text{M}^+$ ).

**1-Chloro-in-Bicyclo[6.3.3]tetradecene (22).** HCl gas was bubbled through a solution of alkene **17** in chloroform for 10 min at –78 °C. The resulting solution was capped in an NMR tube and analyzed by  $^1\text{H}$  NMR spectroscopy:  $\delta$  2.1–0.7 (m, 25 H).

**4-(Benzyloxy)-1-cyclooctanone (24).** 1,4-Cyclooctanediol (100 g, 0.69 mol) was stirred at reflux with NaH (16.6 g, 0.69 mol),  $\text{Bu}_4\text{NBr}$  (10.0 g, 0.03 mol), and benzyl chloride (87.5 g, 0.69 mol) in 500 mL of THF for 16 h. The resulting yellow-orange mixture was diluted with 500 mL of ether and washed with water (400 mL). The ether solution was dried over  $\text{MgSO}_4$  and concentrated. The crude oil was purified by chromatography on silica gel (5:1 hexane/ether as eluent) to yield the benzyloxy alcohol as a clear, colorless oil (60 g, 0.25 mol, 37%, 67% based on recovered starting material):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  7.46–7.11 (m, 5 H), 4.50 (s, 2 H), 3.89–3.86 (s, 1 H), 3.62–3.36 (m, 2 H), 2.51–1.16 (m, 12 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  138.75, 128.0, 127.2, 78.2, 71.3, 69.7, 33.2, 30.1, 29.6, 27.1, 22.7; IR (neat) 3380  $\text{cm}^{-1}$ . 4-(Benzyloxy)-1-cyclooctanol (60 g, 0.25 mol) was stirred at 0 °C in 200 mL of  $\text{CH}_2\text{Cl}_2$ , PCC (70 g, 0.324 mol), powdered molecular sieves (30 g), and sodium carbonate (20 g) until TLC indicated the disappearance of starting material (usually 1 h). The reaction mixture was then diluted with an equal volume of ether and filtered through Florisil. Concentration of the filtered solution yielded pure ketone **24** as a clear, yellow oil (50 g, 0.21 mol, 90%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  7.40–7.18 (m, 5 H), 4.58–4.40 (m, 2 H), 3.59–3.41 (m, 1 H), 2.6–1.2 (m, 12 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,

80 MHz)  $\delta$  217.06, 138.71, 128.31, 127.42, 127.35, 124.54, 77.62, 77.51, 70.09, 40.43, 39.42, 29.72, 28.39, 28.12, 21.98; IR (neat) 1690  $\text{cm}^{-1}$ .

**4-(Benzyloxy)-1-(6-(benzyloxy)hexyl)-1-cyclooctene (25).** A Grignard reagent prepared from 6-(benzyloxy)-1-chlorohexane (40 g, 190 mmol), Mg turnings (4.6 g, 190 mmol), and dry ether (150 mL) was concentrated by high vacuum to a thick paste, diluted with benzene (150 mL), and cooled in an ice-salt bath. Benzyloxy ketone **24** (37.1 g, 160 mmol) was added all at once to the stirred solution. After 10 min, the reaction mixture was diluted with ether (150 mL), washed with 1 N HCl (100 mL) and water (100 mL), dried ( $\text{MgSO}_4$ ), and concentrated. The crude product was purified by column chromatography on silica gel (6:1 ether/hexane as eluent) to give the tertiary alcohol product as a clear oil (38.2 g, 65%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  7.42–7.13 (m, 10 H), 4.52–4.42 (m, 4 H), 3.63–3.35 (m, 3 H), 2.60–0.75 (m, 23 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  174.36, 139.32, 139.01, 138.59, 128.27, 127.55, 127.40, 127.30, 74.40, 74.34, 72.78, 70.36, 70.26, 70.07, 69.80, 41.26, 36.20, 33.31, 32.38, 30.90, 30.01, 29.68, 29.42, 27.99, 26.38, 26.16, 22.88, 22.18, 22.15, 22.03; IR (neat) 3420  $\text{cm}^{-1}$ .

Thionyl chloride (16.7 g, 140 mmol) was added dropwise to a stirred solution of 4-(benzyloxy)-1-(6-(benzyloxy)hexyl)-1-cyclooctanol (58.5 g, 140 mmol), pyridine (22 mL, 280 mmol), and  $\text{CH}_2\text{Cl}_2$  (200 mL) at 0 °C. After 20 min, the reaction mixture was diluted with pentane, washed with water (100 mL), and dried over  $\text{MgSO}_4$ . Concentration of the solution was followed by chromatography of the crude product on silica gel (3% ether/hexane) to yield alkene **25** as a clear, colorless oil (39.4 g, 70%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  3.90–3.71 (m, 1 H), 3.70–3.52 (t, 2 H), 2.05–0.82 (m, 23 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  72.67, 71.71, 63.01, 62.92, 62.83, 60.33, 37.96, 37.65, 37.36, 37.09, 34.85, 34.26, 33.73, 32.77, 32.67, 30.78, 30.51, 29.61, 28.40, 28.13, 27.26, 26.07, 25.65, 25.53, 23.50, 22.24, 15.19.

**4-(6-Oxohexyl)-1-cyclooctanone (26).** Alkene **25** (20 g, 50 mmol) was hydrogenated in a solution of 10:10:1 ethyl acetate/ethanol/acetic acid (50 mL) at 50 psi over Pd-C at room temperature for 24 h. The mixture was then diluted with ether, filtered, and concentrated. Chromatography of the crude product on silica gel (diethyl ether as eluent) gave the pure diol as a viscous, transparent oil (9 g, 77%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  7.42–7.13 (m, 10 H), 4.52–4.42 (m, 4 H), 3.63–3.35 (m, 3 H), 2.60–0.75 (m, 23 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  174.36, 139.32, 139.01, 138.59, 128.27, 127.55, 127.40, 127.30, 74.40, 74.34, 72.78, 70.36, 70.26, 70.07, 69.80, 41.26, 36.20, 33.31, 32.38, 30.90, 30.01, 29.68, 29.42, 27.99, 26.38, 26.16, 22.88, 22.18, 22.15, 22.03; IR (neat) 3420  $\text{cm}^{-1}$ .

The diol from the previous step (1.0 g, 4.4 mmol) in 80 mL of  $\text{CH}_2\text{Cl}_2$  was added dropwise to a stirred mixture containing  $\text{CH}_2\text{Cl}_2$  (100 mL), PCC (3.5 g 16.2 mmol), NaOAc (1.0 g), and powdered molecular sieves. The dark brown suspension was stirred for 2 h and diluted with ether (200 mL). Filtration through Florisil and concentration yielded keto aldehyde **26** as a clear oil (770 mg, 78%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  3.90–3.71 (m, 1 H), 3.70–3.52 (t, 2 H), 2.05–0.82 (m, 23 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  218.0, 202.8, 43.8, 41.9, 41.2, 38.0, 36.2, 30.8, 30.6, 29.3, 26.8, 26.7, 25.3, 22.0; FT-IR ( $\text{CH}_2\text{Cl}_2$ ) 1720, 1690  $\text{cm}^{-1}$ .

**in-Bicyclo[6.4.2]-1-tetradecene (27).** The procedure for the titanium coupling reaction was identical to that specified previously for alkene **17**. The titanium mixture was prepared from 12 g of  $\text{TiCl}_3(\text{DME})_{1.5}$  complex, 6 g of Zn-Cu couple, and 300 mL of DME. Keto aldehyde **26** (370 mg, 1.70 mmol) was added in 50 mL of DME to the reaction flask over 40 h via syringe pump. Standard workup and GC purification of the crude product yielded 72 mg (36%) of alkene **27** as a waxy, white solid (mp 36 °C):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  5.5–5.4 (t, 1 H), 5.2–5.1 (dd, 1 H), 3.35–3.25 (m, 1 H), 2.7–0.8 (m, 22 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  148.6, 142.0, 124.8, 121.2, 40.7, 39.5, 38.1, 35.65, 34.8, 34.4, 33.7, 33.5, 32.7, 31.5, 31.0, 29.9, 28.5, 28.1, 27.6, 26.7, 26.4, 26.2, 26.1, 25.7, 25.4, 25.1, 23.5, 22.0; MS (CI)  $m/e$  192 ( $\text{M}^+$ ).

**in-Bicyclo[6.4.2]-1-tetradecyl Cation (6).** Alkene **27** (3.0 mg, 0.015 mmol) was dissolved in  $\text{CD}_2\text{Cl}_2$  (0.5 mL) in a dry NMR tube under argon at –20 °C, and trifluoromethanesulfonic acid (5.1 mg, 0.036 mmol) was added to the solution via syringe at –20 °C. The tube was then capped and quickly shaken to afford a yellow solution of the cation which proved to be stable below 0 °C:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 200 MHz, –70 °C)  $\delta$  2.8–2.6 (m, 6 H), 2.4–2.2 (m, 6 H), 1.8 (m, 4 H), 1.6–1.4 (m, 4 H), 1.6 (s, 4 H), –6.50 (m, 1 H);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 80 MHz, –70 °C)  $\delta$  178.0, 43.5, 40.0, 37.8, 23.9, 21.6; FT-IR ( $\text{CH}_2\text{Cl}_2$ , –20 °C, trifluoromethanesulfonate salt) 1750  $\text{cm}^{-1}$  (br).

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