

kcal mol<sup>-1</sup> is close to the corresponding outer-sphere barrier (vide supra), it suggests that the transition states for the  $k_1$  and  $k_2$  processes bear a strong resemblance to each other.<sup>45</sup> In other words, the mechanistic distinction between the inner-sphere and outer-sphere electron transfer of ArH<sup>+</sup> and NO lies in the formation ( $K_A$ ) of the (inner-sphere) cation radical pair [ArH<sup>+</sup>, NO] as the *kinetically dominant intermediate*.

### Conclusions

Comparative product studies and time-resolved spectroscopy following the charge-transfer excitation of aromatic complexes with NO<sub>2</sub>Y demonstrate the ion radical pair [ArH<sup>+</sup>, NO<sub>2</sub>] to be a viable intermediate in aromatic nitration, in accord with Olah's thesis of a second reactive intermediate.<sup>3,15</sup> Electron transfer in eq 2 occurs via the inner-sphere mechanism, as judged

(45) Hammond, G. S. *J. Am. Chem. Soc.* 1955, 77, 334.

by the microdynamical behavior of the closely related ion radical pair [ArH<sup>+</sup>, NO] in Scheme IV.<sup>46</sup> As such, other attempts<sup>30</sup> to quantitatively evaluate the electron-transfer mechanism by the indiscriminate application of Marcus theory for *outer-sphere* electron transfer are conceptually flawed.<sup>47</sup>

*I thank my colleagues, especially S. Sankararaman, E. K. Kim, T. M. Bockman, and K. Y. Lee, for their tireless efforts to fathom the intricacies of electron-transfer dynamics and mechanisms of the nitrogen oxides, and the National Science Foundation, Robert A. Welch Foundation, and Texas Advanced Research Program for financial support.*

(46) For the inner-sphere structures of such nonbonded donor-acceptor complexes, see ref 42. Analogously, the inner-sphere character of the ion radical pair in nitration is likely to be reflected in a bent NO<sub>2</sub> moiety in the nonbonded structure of I. Further studies are in progress to reconcile the first-order kinetics in Table I and Figure 4b.

(47) For an early caveat, see the following: Fukuzumi, S., et al., ref 38. Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 1227.

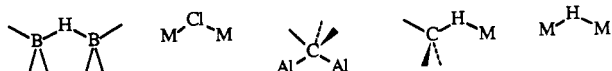
## Three-Center, Two-Electron C-H-C Bonds in Organic Chemistry<sup>†</sup>

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Received October 10, 1991 (Revised Manuscript Received November 6, 1991)

To organic chemists, covalent bonding is synonymous with the sharing of two electrons between two atomic centers. The stable substances we usually work with contain only such two-center, two-electron bonds: C-H, C-C, C-O, and so forth. Inorganic and organometallic chemists, however, are used to dealing with a much richer diversity of bonding patterns that often includes the sharing of two electrons between *three* atomic centers. Such three-center, two-electron bonds (3c-2e) are particularly common in the boron hydrides, but are also found in bridged metal halides, bridged metal alkyls, metal-hydrogen agostic interactions, and many other systems.

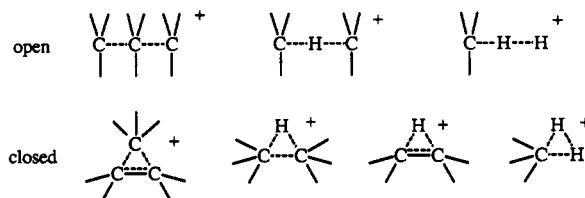


Three-center, two-electron bonding is not, of course, limited to inorganic and organometallic chemistry. Such bonding also occurs in organic chemistry, but the instances of its occurrence are relatively few, and the substances that contain these bonds are relatively unstable.<sup>1</sup> Several kinds of 3c-2e bonds are possible

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Thomas Lectka, a native of Detroit, MI, received his B.A. from Oberlin College in 1985 and his Ph.D. from Cornell University in 1991. Following his doctoral work, the subject of which forms the basis of this Account, he spent a year as an Alexander von Humboldt Fellow in the laboratory of Professor Rolf Gleiter at Heidelberg and then moved to Harvard University for further postdoctoral work with David Evans. His research interests include a blend of synthetic organic, physical organic, and computational problems.

in organic chemistry, and it is useful to distinguish between the "open" or "unsupported" situation and the "closed" or "supported" one.<sup>2</sup> Open 3c-2e bonds are those wherein the geometry is roughly linear so that there is negligible bonding interaction between the terminal atoms. Closed 3c-2e bonds are those wherein the geometry is acutely triangular so that there is a bonding interaction among all three atoms. Of course, the two situations are merely the extremes of a bonding continuum. Note that organic substances showing 3c-2e bonding must be cations and that one or more of the atoms involved—either carbon or hydrogen—must be "hypervalent". That is, one or more of the carbon atoms must be pentavalent or one or more of the hydrogens must be divalent.



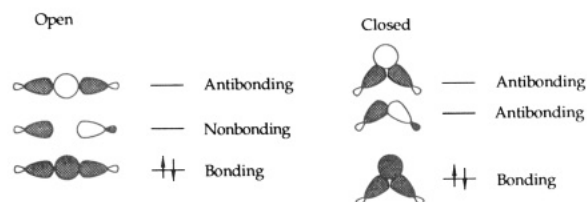
A molecular orbital description of 3c-2e bonding shows a doubly occupied bonding MO, along with

<sup>†</sup> It is a great pleasure to dedicate this paper to my friend and colleague Professor Joseph Bunnett, whose vision and hard work made this journal the outstanding success that it is today.

(1) For reviews of three-center, two-electron bonds in organic chemistry, see: (a) Olah, G. A.; Surya Prakash, G. K.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley-Interscience: New York, 1987. (b) DeKock, R. L.; Bosma, W. B. *J. Chem. Educ.* 1988, 65, 194-197.

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

unoccupied nonbonding and/or antibonding MOs. To take the C–H–C bond as an example,  $\Psi_2$  is a nonbonding MO in the open case because the carbons are too distant to interact. In the closed case, however,  $\Psi_2$  is antibonding because the two carbon-centered orbitals interact unfavorably. Furthermore, the occupied bonding MO is lower in energy in the closed case than in the open case because of a favorable carbon–carbon interaction, making the closed geometry energetically preferred over the open geometry in the absence of overriding steric factors. This preferred bent geometry of several M–H–M bonds has been clearly shown in neutron-diffraction studies.<sup>2</sup>

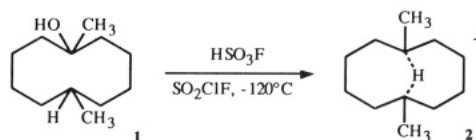


Of the closed situations involving C and H, the closed C–C–C 3c–2e bond is the most well-known and the most extensively studied because of its occurrence in various substituted norbornyl cations.<sup>3</sup> Large amounts of data have been gathered for these cations, and X-ray crystal structures have been obtained.<sup>4</sup> The closed C–C–H, or “protonated ethane”, bond has been detected in the mass spectrometer, and an infrared spectrum of  $C_2H_7^+$  has been published.<sup>5</sup> The closed C–H–H bond is also well studied, and mass spectroscopic evidence for its occurrence in  $CH_5^+$  has been reported.<sup>6</sup> Such bonding almost certainly also occurs in alkane protonolysis reactions,<sup>7,8</sup> about which more will be said below.

Of the open possibilities, both C–C–C and C–C–H 3c–2e bonds appear to be unknown; no evidence has been obtained for either type to the best of our knowledge. The open C–H–C bond is quite different, however, and proposals for its occurrence in the hydride-transfer rearrangements of carbocations go back several decades.<sup>9</sup> NMR evidence for the existence of hydrido-bridged carbocations containing C–H–C 3c–2e bonds was first obtained in 1978 by Sorensen,<sup>10</sup> who was able to show convincingly that the 1,6-dimethyl-1-cyclodecyl cation (2) and several related ions contain stable C–H–C bonds when generated from the corresponding alcohols by treatment with fluorosulfonic acid at  $-120^\circ C$ .<sup>11</sup>

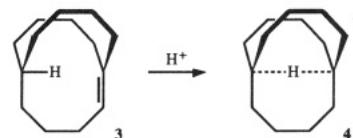
Among the most convincing pieces of evidence cited by Sorensen in support of his structural assignment is the low-temperature  $^1H$  NMR spectrum of 2, which

shows the bridging hydrogen at  $\delta -3.9$  coupled to the two carbons with  $J = 35 \pm 2$  Hz. Although unexpected at the time, this unusual upfield resonance turns out to be characteristic of all systems with 3c–2e C–H–C bonds. Further NMR evidence for the structure assignment was obtained by applying the equilibrium deuterium isotope effect criterion of Saunders.<sup>12</sup> When cation 2 containing one  $CD_3$  group in place of a  $CH_3$  group was prepared, the  $^{13}C$  chemical shift difference between the two terminal carbons of the C–H–C bond was only 0.60 ppm, a value characteristic of a static (bridged) system rather than of a rapidly equilibrating mixture of classical cations.



The dimethylcyclodecyl ion 2 and related substances show clear evidence of 3c–2e bonding, but are troublesome to study because of their instability at normal temperatures. Ion 2, for example, slowly rearranges to an isomeric bridged ion when warmed to  $-100^\circ C$  and undergoes slow decomposition above  $-70^\circ C$ . Is it possible to design and synthesize a stable organic ion with 3c–2e bonding? Precedent suggests that the bridged cyclodecyl system has a nearly optimum geometry for 3c–2e bonding, flawed only because decomposition pathways involving loss of the bridging hydrogen are open to it. What is needed is a rigid, cage-like structure that retains the geometry of the bridged cyclodecyl ring system but that prevents loss of the bridging hydrogen.

A study of molecular models, coupled with the serendipitous appearance of an Account by Alder describing his work on the chemistry of medium-ring bicycloalkanes,<sup>13</sup> led us in the early 1980s to the notion that the *in*-bicyclo[4.4.4]tetradecyl cation (4) should be ideal.<sup>14</sup> All rings are 10-membered, the inside hydrogen is permanently held within range of the carbon atom at the opposite bridgehead, and the caged structure should make it sterically impossible for the inside hydrogen to escape. In space-filling models, in fact, the inside hydrogen is so well enclosed by the three tetramethylene bridges that it is not even visible.



### Synthesis of *in*-Bicyclo[4.4.4]-1-tetradecene (3)

Our plan for the synthesis of cation 4 was to prepare it by protonation of the corresponding bridgehead alkene 3, itself prepared by titanium-induced carbonyl coupling<sup>15</sup> of 6-(4-oxobutyl)cyclodecanone (5). Though

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

(13) Alder, R. W. *Acc. Chem. Res.* 1983, 16, 321–327.

(14) Preliminary communication: McMurry, J. E.; Hodge, C. N. *J. Am. Chem. Soc.* 1984, 106, 6450. Full paper: McMurry, J. E.; Lectka, T.; Hodge, C. N. *J. Am. Chem. Soc.* 1989, 111, 8867–8872.

(15) For reviews of the titanium-induced carbonyl coupling reaction, see: (a) McMurry, J. E. *Acc. Chem. Res.* 1983, 16, 405–411. (b) McMurry, J. E. *Chem. Rev.* 1989, 89, 1513–1524. (c) Lenoir, D. *Synthesis* 1989, 883–897.

(3) For a wrapup, see: (a) Brown, H. C. *Acc. Chem. Res.* 1983, 16, 432–440. (b) Olah, G. A.; Surya Prakash, G. K.; Saunders, M. *Acc. Chem. Res.* 1983, 16, 440–448.

(4) Laube, T. *J. Am. Chem. Soc.* 1989, 111, 9224–9232.

(5) Yeh, L. I.; Price, J. M.; Lee, Y. T. *J. Am. Chem. Soc.* 1989, 111, 5597–5604.

(6) Field, F. H.; Munson, M. S. B. *J. Am. Chem. Soc.* 1965, 87, 3289.

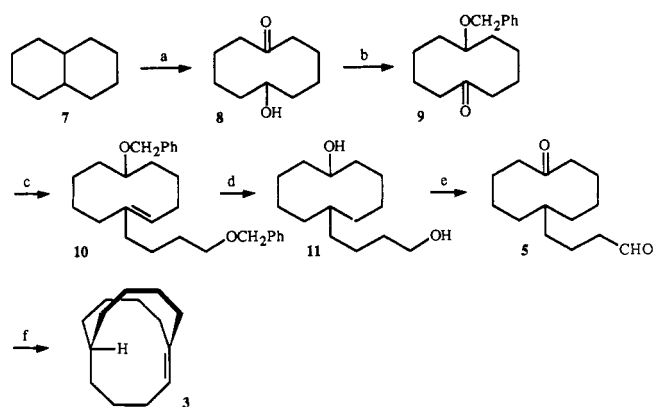
(7) Olah, G. A.; Halpern, Y.; Shen, J.; Mo, Y. K. *J. Am. Chem. Soc.* 1973, 95, 4960–4970.

(8) Schlosberg, R. H.; Siskin, M.; Kosci, W. P.; Parker, F. J. *J. Am. Chem. Soc.* 1976, 98, 7723–7725.

(9) Prelog, V.; Traynham, J. G. *Molecular Rearrangements*; de Mayo, P., Ed.; Interscience: New York, 1963; Vol. 1, p 593.

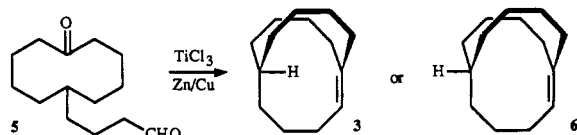
(10) Kirchen, R. P.; Sorensen, T. S. *J. Chem. Soc., Chem. Commun.* 1978, 769.

(11) Kirchen, R. P.; Ranganayakulu, K.; Rauk, A.; Singh, B. P.; Sorensen, T. S. *J. Am. Chem. Soc.* 1981, 103, 588–596.

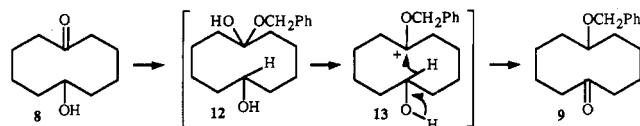
Scheme I<sup>a</sup>

<sup>a</sup>(a) O<sub>2</sub>, *hν*, then H<sub>2</sub>SO<sub>4</sub>, 8%; (b) PhCH<sub>2</sub>OH, HCl, 66%; (c) PhCH<sub>2</sub>O(CH<sub>2</sub>)<sub>4</sub>MgCl, benzene, Bu<sub>4</sub>NBr, 75%; (d) TsOH, benzene, 77%, then H<sub>2</sub>, Pd/C, 87%; (e) PCC, CH<sub>2</sub>Cl<sub>2</sub>, NaOAc, 95%; (f) TiCl<sub>3</sub>(DME)<sub>1.5</sub>, Zn-Cu; DME, 30%.

straightforward in appearance, there are two potential problems with this plan. One is that alkene **3** is highly strained and the cyclization of **5** to **3** might therefore be difficult. The second and perhaps even more serious problem is that the cyclization might yield the alternative *out* isomer **6** rather than the desired *in* isomer **3**. Molecular mechanics calculations predict, however, that **3** is less strained than **6** by 7.4 kcal/mol, giving us some confidence that the cyclization should give the correct product.



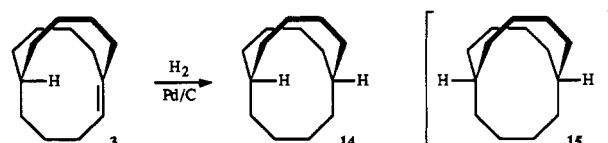
The synthesis of keto aldehyde **5** and its cyclization to yield **3** are shown in Scheme I. Starting from decalin (**7**), photosensitized oxygenation and acid-catalyzed rearrangement of the intermediate hydroperoxide<sup>16</sup> gave keto alcohol **8**, which was protected as its benzyl ether **9** by reaction with benzyl alcohol and dry HCl. (Parenthetically, this protection probably occurs by a transannular hydride transfer step, **13** → **9**, which itself involves a hydride-bridged, 3c-2e intermediate.)



Grignard addition to **9** of the four-carbon [4-(benzyloxy)butyl]magnesium chloride gave a tertiary alcohol intermediate, which was dehydrated by treatment with *p*-toluenesulfonic acid in benzene and then subjected to deprotection/reduction by hydrogenation over a palladium catalyst. The resultant saturated diol **11** was oxidized with pyridinium chlorochromate (PCC), and keto aldehyde **5** was then treated with a slurry of Ti(0) prepared by reduction of TiCl<sub>3</sub>·(DME)<sub>1.5</sub> with Zn/Cu in refluxing dimethoxyethane.<sup>17</sup> After careful optimization of the reaction conditions, a 30% yield of the pure *in*-bicyclo[4.4.4]-1-tetradecene (**3**) was obtained as a translucent white solid.

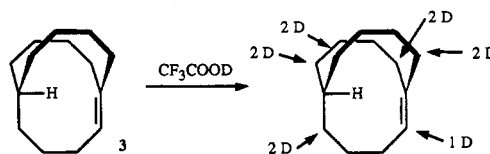
(16) Mijs, W. J.; DeVries, K. S.; Westra, J. S.; Angad-Gaur, H. A.; Smidt, J.; Vriend, J. *Recl. Trav. Chim. Pays-Bas* 1968, 87, 580-584.  
(17) McMurry, J. E.; Lectka, T.; Rico, J. G. *J. Org. Chem.* 1989, 54, 3748-3749.

Proof that the bicyclopentadecene cyclization product was indeed the *in* isomer **3** was obtained by catalytic hydrogenation over a palladium catalyst. The bicycloalkane (**14**) obtained from this reduction showed a <sup>13</sup>C NMR spectrum of six lines, consistent with the presence of a 3-fold axis as the only symmetry element (C<sub>3</sub>). Had the alternative *out* isomer **6** been formed in the cyclization, catalytic reduction would have yielded alkane **15**, which would be expected to show only three lines in its <sup>13</sup>C NMR spectrum as a result of D<sub>3h</sub> symmetry. Confirmation of this assignment was obtained by <sup>1</sup>H NMR spectroscopy of **14**, which showed two one-proton resonances at δ 2.5 and 1.13, corresponding to the two different bridgehead hydrogens. Were **15** the structure, only a single bridgehead resonance would be expected.



### Synthesis and Characterization of the *in*-Bicyclo[4.4.4]tetradecyl Cation (**4**)

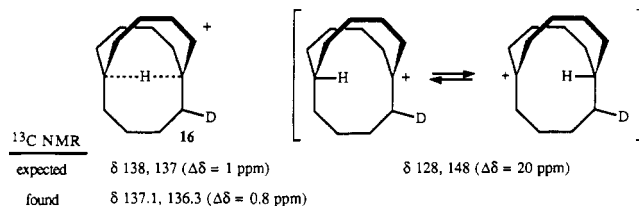
Our initial attempts to prepare a cation from **3** centered on the idea of adding HCl to generate a tertiary alkyl chloride, which we hoped might ionize under mild conditions. To our surprise, however, we found that alkene **3** was inert to electrophilic addition reactions: Only starting material was recovered after treating **3** with dry HCl in a variety of solvents. Upon treatment with deuterated acids, however, a more interesting result was obtained. Reaction with CF<sub>3</sub>COOD at room temperature, followed by quenching with NaHCO<sub>3</sub>, led to the nearly instantaneous incorporation of 11 deuterium atoms into the molecule at the positions next to both bridgehead carbons. This result can only be explained by assuming a rapid protonation/deprotonation equilibrium that makes the six positions next to both bridgeheads equivalents.



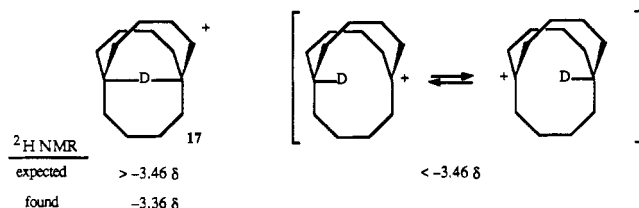
An even more remarkable result was obtained when alkene **3** was dissolved in CF<sub>3</sub>COOH or CF<sub>3</sub>SO<sub>3</sub>H at room temperature and the resultant solution was examined by NMR. The <sup>1</sup>H NMR spectrum showed only three absorptions: two broad 12-proton peaks at δ 2.5 and 1.9 and a broad 1-proton singlet at δ -3.46. The <sup>13</sup>C NMR spectrum showed only three absorptions, at δ 19.3 (t), 41.6 (t), and 139.3 (d, J<sub>C-H</sub> = 47 Hz). All of this spectroscopic evidence is in full agreement with Sorensen's previous findings and with the conclusion that we have generated a bridged ion. As hoped, though, the stability of ion **4** is greatly enhanced over that of previously known species. In fact, solutions of **4** are stable for several weeks at room temperature or below, undergoing slow decomposition only when heated.

Further evidence for the existence of a 3c-2e C-H-C bond in cation **4** was found by preparing the mono-deuterated analogue **16** and measuring its <sup>13</sup>C NMR spectrum. Applying Saunders' deuterium isotope effect

criterion,<sup>12</sup> we would expect different results to be obtained depending on whether ion 4 has a symmetrical bridged structure or two unsymmetrical but rapidly equilibrating classical structures. We would expect the chemical shifts of the two bridgehead carbon atoms to be separated by only a slight difference in the symmetrical structure ( $\Delta\delta \approx 1$  ppm) but by a much larger difference in the equilibrating structures ( $\Delta\delta \approx 20$  ppm). The experimental value, determined by treating 3 with  $\text{FSO}_3\text{D}$  at  $-92^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$ , was  $\Delta\delta \approx 0.8$  ppm. This measurement showed a negative temperature dependence, decreasing to 0.2 ppm at  $0^\circ\text{C}$ .



Still further NMR evidence for 3c-2e bonding in cation 4 was obtained with the  $\Delta\delta(^1\text{H},^2\text{H})$  test of Altman and Forsén<sup>18</sup> for probing the shape of the potential energy surface of an X-H-X bond. If a downfield shift of the hydrogen in the NMR spectrum is observed on going from the protio substrate (C-H-C) to the deuterio substrate (C-D-C), then a single-minimum potential surface characteristic of a 3c-2e bond is indicated. If no shift or an upfield shift is observed, then a double-minimum potential surface characteristic of equilibrating classical ions is indicated. When the necessary *in*-deuterio substrate 17 was prepared and its <sup>2</sup>H NMR spectrum obtained, a downfield shift of 0.10 ppm was found, exactly as expected.



In addition to the NMR evidence, IR spectroscopy provided yet further proof for the presence of a symmetric 3c-2e bond in cation 4. Reaction of alkene 3 with trifluoromethanesulfonic acid in  $\text{CH}_2\text{Cl}_2$  at room temperature gave a cation solution that showed a strong absorption at  $2113\text{ cm}^{-1}$ , along with normal C-H and C-C bands. Similar work on the deuterated cation 17 showed an absence of the absorption at  $2113\text{ cm}^{-1}$  but the presence of a new band at  $1558\text{ cm}^{-1}$ , with all other bands in the spectrum essentially unaffected by the isotopic substitution. The isotropic shift of  $565\text{ cm}^{-1}$  on changing from *in*-protio to *in*-deuterio allows us to assign the  $2113\text{-cm}^{-1}$  band to an asymmetric C-H-C stretching motion, again consistent with a symmetric single-minimum potential surface for the 3c-2e bond.<sup>19</sup>

A vibrational analysis of the observed C-H-C asymmetric stretch was carried out by approximating the three-center bond as a classical linear three-body oscillator with negligible coupling to other molecular vibrations.<sup>20</sup> We calculate a force constant of  $1.26 \times 10^5$

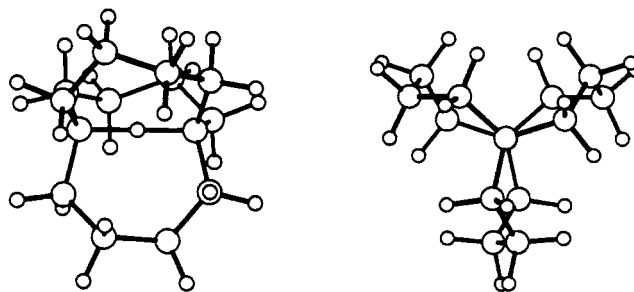


Figure 1. Optimized (AM1) structure of the bicyclo[4.4.4]-tetradecyl cation.

dyn/cm for the three-center C-H-C bond, a value that compares to force constants in the range  $4.8\text{--}5.9 \times 10^5$  dyn/cm for normal two-center C-H bonds.

Perhaps the most dramatic measure of the extraordinary stability of cation 4 comes from simple tests to determine how strong an acid is needed to protonate the double bond in alkene 3. By dissolving the alkene in acids of different strengths and analyzing the extent of protonation by NMR, we determined that, even in pure acetic acid, bicyclo[4.4.4]-1-tetradecene is approximately 50% protonated at room temperature. In other words, alkene 3 is nearly as strong a base as acetate ion, and cation 4 is nearly as weak an acid as acetic acid: truly remarkable behavior for a hydrocarbon.

Both semiempirical (AM1) and ab initio calculations fully optimized at the 3-21G level have been carried out on cation 4. The calculated results predict a  $D_3$  symmetric structure with linear C-H-C geometry and a broad, shallow single-minimum potential surface. The C-H bond distance is calculated to be in the range 1.31 Å (AM1) to 1.22 (3-21G), substantially longer than the value for a normal two-electron C-H bond. The optimized structure is shown in Figure 1.

#### Other Stable Ions with 3c-2e C-H-C Bonds

One of the more puzzling pieces of data to come from NMR studies on substances with 3c-2e C-H-C bonds is the remarkable upfield shift experienced by the central hydrogen atom. The substances are *cations*, yet the central hydrogen is more strongly shielded than hydrogens in neutral molecules. This shielding presumably reflects the electron distribution in the ion and indicates an unusually high electron density on the hydrogen in the three-center bond. As noted previously, however, the amount of orbital overlap in the three-center bond depends on the C-H-C angle and should be greater for bent bonds than for linear ones. It therefore occurred both to us and to Sorensen to prepare a series of ions in which the C-H-C angle was progressively bent and to examine the effect of that bending on the electron distribution in the three-center bond.

Assuming that a caged structure is necessary to impart thermal stability to three-center ions, the C-H-C angle within the cage can be varied by changing the sizes of the three bridges. Sorensen therefore prepared a series of ions based on a bridged bicyclo[3.3.1]nonyl ring as in the general structure 18.<sup>21</sup> Our own approach was to build a series of bicyclo[*x.y.z*]alkyl rings as in the general structure 19.<sup>22</sup> In both approaches, the ions

(18) Altman, L. J.; Laungani, D.; Gunnarsson, G.; Wennerström, H.; Forsén, S. *J. Am. Chem. Soc.* 1978, 100, 8264-8266.

(19) Emsley, J. *Chem. Soc. Rev.* 1980, 9, 91-124.

(20) Wiberg, K. B. *Physical Organic Chemistry*; John Wiley and Sons: New York, 1964; pp 141-162.

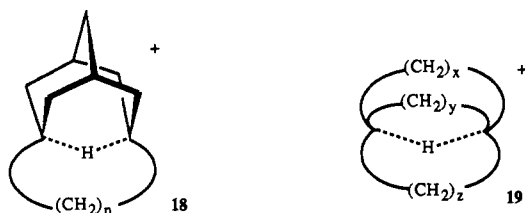
(21) Sorensen, T. S.; Whitworth, S. M. *J. Am. Chem. Soc.* 1990, 112, 8135-8144.

Table I  
<sup>1</sup>H NMR Data for Cations 18 and 19

cation	$\delta$ (inside H)	C-H-C angle, deg	stability, °C
18 ( $n = 5$ )	-5.64	161	rt <sup>a</sup>
18 ( $n = 6$ )	-4.56	129	rt
18 ( $n = 7$ )	-1.46		<-10
18 ( $n = 8$ )	0.07		<-25
19[4.4.4]	-3.46	180	rt
19[5.4.4]	-4.20	161	rt
19[6.3.3]	-6.42	131	rt
19[6.4.2]	-6.5	113	<10

<sup>a</sup> Room temperature.

were generated by protonation of the corresponding bridgehead alkenes prepared by intramolecular titanium-induced carbonyl coupling of the appropriate keto aldehyde precursors.



Of the various possibilities based on the bridged bicyclo[3.3.1]nonyl ring 18, cations with  $n = 5-8$  were prepared, and relevant NMR data are summarized in Table I. Cation 18 ( $n = 8$ ) was prepared by protonation of the corresponding bridgehead alkene at  $-80$  °C with  $\text{FSO}_3\text{H-SbF}_5$  in  $\text{SO}_2\text{ClF}$  and found to be thermally stable below  $-20$  °C. The inside hydrogen absorbs at  $\delta$  0.07 in the <sup>1</sup>H NMR spectrum, however, indicating a classical carbocation structure without a 3c-2e bond. Cation 18 ( $n = 7$ ) was also prepared in  $\text{FSO}_3\text{H-SbF}_5/\text{SO}_2\text{ClF}$  and found to be thermally stable below  $-10$  °C. At  $-25$  °C, the inside hydrogen absorbs at  $\delta$  -1.46, probably indicative of partial and unsymmetrical 3c-2e bond formation. Cation 18 ( $n = 6$ ) could be prepared in several acidic solutions although not in pure  $\text{CF}_3\text{COOH}$ . The ion is thermally stable for several days at room temperature and shows an absorption at  $\delta$  -4.56 for the inside hydrogen, indicating the presence of a 3c-2e bond. Cation 18 ( $n = 5$ ) was the most stable of the series and could be prepared in  $\text{CF}_3\text{COOH}$  at room temperature. The absorption of the inside hydrogen at  $\delta$  -5.64 clearly indicates 3c-2e bonding.

Of the various bicyclo[ $x.y.z$ ]alkyl possibilities based on structure 19, three cations were prepared in addition to the bicyclo[4.4.4]tetradecyl ion studied previously (19[4.4.4] = 4). These additional ions are the bicyclo[5.4.4]pentadecyl ion, the bicyclo[6.3.3]tetradecyl ion, and the bicyclo[6.4.2]tetradecyl ion. NMR data for the bicyclo[ $x.y.z$ ] ions 19 are summarized in Table I.

All four of the bicyclo[ $x.y.z$ ] cations listed in Table I appear to contain 3c-2e bonds, as judged by the upfield absorption of the inside hydrogen. Both the [5.4.4] and the [6.3.3] ions can be prepared from the corresponding bridgehead alkenes by protonation with  $\text{CF}_3\text{COOH}$ , and both are stable at room temperature. Cation 19[6.3.3] should be roughly comparable in geometry to 18 ( $n = 6$ ), but the chemical shifts of the two are appreciably different. The 3c-2e hydrogen in 19-

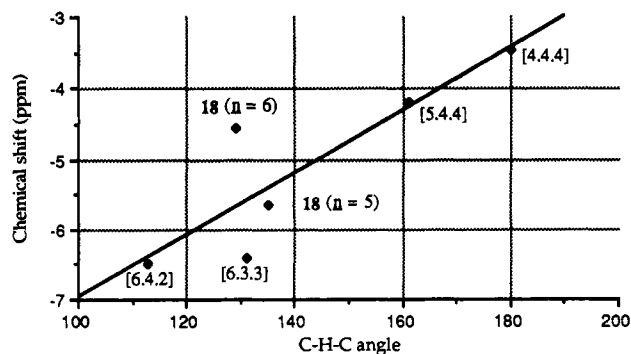


Figure 2. A plot of chemical shift for the inside hydrogen versus the calculated C-H-C bond angle for the series of cations 18 and 19 listed in Table I.

[6.3.3] absorbs at  $\delta$  -6.42, among the highest field absorptions we have yet found. Ion 19[6.4.2] also displays some unusual behavior in that it is less stable than other bridged ions, decomposing above  $10$  °C, yet it has an unusually high field absorption at  $\delta$  -6.5 for its inside hydrogen. Furthermore, the NMR spectrum is temperature dependent, with two different high-field absorptions ( $\delta$  -6.4 and -6.5) present at  $-50$  °C.

Precise values for the C-H-C angles in the various cations are not known and cannot be obtained from available information, but estimates can be made from calculations. Assuming that the C-H-C interaction itself contributes in only a minor way to the overall energy of an ion and that the geometry of an ion is therefore due largely to normal steric and electronic factors, it should be possible to obtain fairly accurate minimum-energy conformations simply by molecular mechanics calculations.

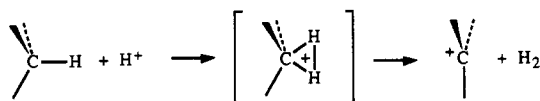
In the case for which we were able to test this conformational assumption, that of cation 4, the results were satisfactory. Thus, when the central hydrogen is constrained to be equidistant from the two bridgehead carbons and the experimentally obtained value of  $1.26 \times 10^5$  dyn/cm is used for the C-H force constant, molecular mechanics calculations on cation 4 predict a  $C_3$  symmetric structure with a linear C-H-C bond and C-H distance of 1.31 Å. For comparison, AM1 calculations predict a C-H distance of 1.31 Å, STO-3G calculations predict a C-H distance of 1.25 Å, and 3-21G calculations predict a C-H distance of 1.22 Å. The results of molecular mechanics calculations on other cations with 3c-2e bonds are given in Table I and indicate a substantial amount of C-H-C bending in most cases.

A plot of calculated C-H-C bond angle versus chemical shift for the inside hydrogen is shown in Figure 2. The correlation is a reasonably good one, with the exception of one outlier in the case of 18 ( $n = 6$ ). There is reason to suspect, however, that the reported chemical shift for this cation may not be accurate. Sorensen has noted that the chemical shift of the inside hydrogen in this substance is temperature dependent and can be interpreted in terms of two cationic species, a major and a minor population. At moderate temperatures, a rapid nondegenerate exchange between the two structures occurs, but at lower temperatures, line broadening is seen and the inside hydrogen moves to higher field. Thus the major cationic species with a 3c-2e bond must have an even higher chemical shift than  $\delta$  -4.56, as predicted on the basis of the correlation in Figure 2.

The reasons for the correlation of chemical shift with H-C-H angle shown in Figure 2 are not yet clear. The results suggest that electron density on the bridging hydrogen increases as the C-H-C angle becomes more acute and the strength of the three-center, two-electron bonding interaction increases. Both semiempirical and ab initio calculations predict, however, that the opposite trend should be observed. Further studies and higher level calculations are needed to resolve the discrepancy.

### 3c-2e C-H-H Bonds in Alkane Protonolysis Reactions

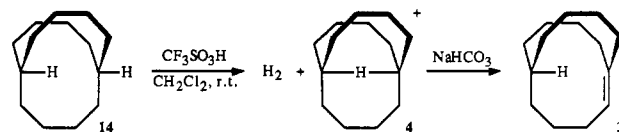
As noted above, 3c-2e C-H-H bonds are much less well-known than their C-H-C counterparts, and no stable substances with this kind of bond have been prepared. Nevertheless, 3c-2e C-H-H bonding is undoubtedly widespread and almost certainly occurs during alkane protonolysis reactions in which a carbocation is generated by treatment of an alkane with strong acid.<sup>23</sup>



Although the alkane protonolysis reaction appears simple, its mechanism has been the subject of controversy for more than two decades, largely because a nonstoichiometric amount of hydrogen is usually produced,<sup>24</sup> particularly when strong protic acid/Lewis acid combinations such as HSbF<sub>6</sub> are used. One explanation<sup>25</sup> for the diminished amount of H<sub>2</sub> produced is that the pentacoordinate RH<sub>2</sub><sup>+</sup> intermediate is intercepted and reduced by SbF<sub>5</sub> prior to the escape of H<sub>2</sub>, but this explanation has been challenged.<sup>26</sup>

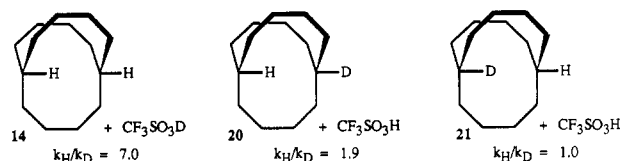
Since the ease of carbocation formation should depend on the stability of the cation being formed, and since 4 is one of the most stable carbocations known, it occurred to us that protonolysis of alkane 14 might be unusually easy, perhaps even taking place with normal protic acids and without the problematic HX/MX<sub>n</sub> combination. If so, it might provide new information about the general reaction.

The protonolysis reaction of 14 does in fact proceed under remarkably mild conditions.<sup>30</sup> Warming a dilute solution of 14 to 40 °C in glacial acetic acid resulted in the slow disappearance of 14 and the appearance of alkene 3. The reaction was faster if CF<sub>3</sub>COOH was used, and faster still if carried out with trifluoromethanesulfonic acid in dichloromethane. When alkane 14 dissolved in a small amount of CH<sub>2</sub>Cl<sub>2</sub> was added to CF<sub>3</sub>SO<sub>3</sub>H at 0 °C, visible gas evolution occurred, and 90% of the theoretical amount of H<sub>2</sub> was collected in 1 h. A clean solution of cation 4 was produced, as



identified by NMR, and a 75% yield of alkene 3 was obtained on quenching of the solution with NaHCO<sub>3</sub>.

Further information about the protonolysis reaction was obtained by carrying out several deuterium isotope experiments. When unlabeled substrate 14 was allowed to react with deuterated trifluoromethanesulfonic acid, CF<sub>3</sub>SO<sub>3</sub>D, at 0 °C, a large solvent kinetic isotope effect,<sup>27</sup>  $k_H/k_D = 7.0$ , was noted as determined by disappearance of starting material (GLC analysis) and appearance of alkene 3. Similar experiments using unlabeled CF<sub>3</sub>SO<sub>3</sub>H on the *out*-deuterio alkane 20 at 0 °C gave a primary isotope effect of  $k_H/k_D = 1.9$ , and reaction of unlabeled CF<sub>3</sub>SO<sub>3</sub>H on the *in*-deuterio alkane 21 at 0 °C gave no detectable remote isotope effect.<sup>28</sup>



These three results together imply a nonconcerted multistep reaction whose rate-limiting step involves breakage of both the alkane C-H bond and the acid O-H bond. If the reaction were concerted, one would expect a measurable remote isotope effect on 21. If loss of H<sub>2</sub> were rate-limiting, one would expect both a small solvent isotope effect on the reaction of 14 with CF<sub>3</sub>SO<sub>3</sub>D and some exchange of the outside bridgehead hydrogen. No such exchange was observed, however, when the reaction of 14 with deuterated acid was allowed to go to partial completion and the recovered starting material was analyzed by mass spectroscopy.

The picture of alkane protonolysis that emerges from this study is fully consistent with an RH → RH<sub>2</sub><sup>+</sup> → R<sup>+</sup> + H<sub>2</sub> pathway involving an intermediate with a 3c-2e C-H-H bond. Although we are not aware of any suitable model to use for comparison, it should be noted that the primary kinetic isotope effect observed in the reaction of 20 is rather small, as might be expected for a nonlinear transition state leading to a closed, triangular C-H-C bond.<sup>29</sup>

### Conclusions

Though not as common as in organometallic and inorganic chemistry, there is no doubt that three-center, two-electron bonds exist in organic chemistry. Given the proper choice of substrates and a properly designed system that enforces a necessary proximity of the three atomic centers, substances with 3c-2e bonds can even be stable under normal conditions and can be examined by normal solution spectroscopic techniques.

(27) For a discussion of solvent isotope effects, see: *Isotope Effects on Chemical Reactions*; Buncl, E., Lew, C. C., Eds.; Elsevier: New York, 1987.

(28) For a discussion of remote isotope effects, see: Sunko, D. E.; Boric, S. *Isotope Effects on Chemical Reactions*; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand: New York, 1970; p 172.

(29) More O'Ferrall, R. A. *J. Chem. Soc. B* 1970, 785-790.

(30) McMurry, J. E.; Lectka, T. *J. Am. Chem. Soc.* 1990, 112, 869-870.

(23) For reviews, see: (a) Fabre, P.-L.; Devynck, J.; Tremillon, B. *Chem. Rev.* 1982, 82, 591-614. (b) Brouwer, D. M.; Hogeveen, H. *Prog. Phys. Org. Chem.* 1972, 9, 179-240. (c) Olah, G. A.; Surya Prakash, G. K.; Sommer, J. *Superacids*; Wiley-Interscience: New York, 1985; pp 243-266. (d) Olah, G. A.; Surya Prakash, G. K.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley-Interscience: New York, 1987; pp 218-233.

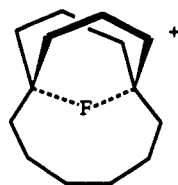
(24) Stoichiometric hydrogen formation has also been reported: Bassir, M.; Torck, B.; Hellin, M. *New J. Chem.* 1987, 11, 437-441.

(25) Ledford, T. H. *J. Org. Chem.* 1979, 44, 23-25.

(26) Kirchen, R. P.; Sorensen, T. S.; Wagstaff, K.; Walker, A. M. *Tetrahedron* 1986, 42, 1063-1070.



What lies in the future for work in this field? Certainly it is possible to imagine other kinds of 3c-2e bonds that might be stabilized according to the general principles described in this Account. Among the possibilities, stable C-F-C bonds and (the ultimate goal of many physical organic chemists over the past half century) C-C-C bonds are well worth reaching for. We have already identified and carried out preliminary calculations on systems that look attainable: the *in*-fluorobicyclo[6.3.3]tetradecyl system, for example, looks sterically and electronically ideal to support 3c-2e C-F-C bonding. All that is needed now is to reduce the idea to practice.



The *in*-fluorobicyclo[6.3.3]tetradecyl cation.  
A stable ion with a 3c-2e C-F-C bond?

*This work was supported financially by the donors of the Petroleum Research Fund, administered by the American Chemical Society, through Grant 15406-AC1 and by the National Science Foundation through Grants CHE-8615638 and CHE-8917619. T.L. was the recipient of a Division of Organic Chemistry Fellowship awarded by the American Chemical Society and sponsored by the Monsanto Company.*