J. Am. Chem. Soc. 1993, 115, 77-81

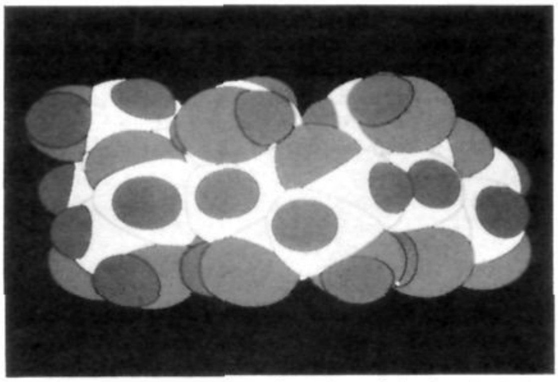

Figure 3. Energy-minimized conformation of the dextrin chain; the trimer molecule is illustrated. The small gray balls are hydrogens, the large white ones are carbons, and the large gray ones are oxygen atoms.

(Figure 3). The α-1*a*,4*e*-linkage constrains the chain into generating a hydrophobic surface; in contrast, the α-1,6-linked and the β-1,4-linked chains are only hydrophilic. Our calculations have also revealed the presence of amphiphilic surfaces in β-1,3- and β-1,4-D-galactans, α-1,2-, α-1,4-, and β-1,3-D-mannans, and β-1,3- and α-1,4-D-xylans. The β-1,4-D-glucan (cellulose) and β-1,4-D-xylan that we have used in this paper are only hydrophilic.

The concept of hydrophobicity in sugars, unexpected as it may seem, is important to many aspects of their molecular interactions, such as with lectins and with antibodies, and in cell surface events. Johnson et al.[18] have reviewed crystallographic evidence for the occurrence of apolar contacts between oligosaccharide chains and enzymes such as lysozyme, phosphorylase, and the amylases. Surolia and co-workers[19,20] have provided thermodynamic evidence for hydrophobic interactions between sugars and proteins in aqueous solution. Lemieux et al.[21,22] have shown a pattern of interactions between oligosaccharides and antibodies that involves the recognition of an amphiphilic surface presented to the protein by the sugar chain. It would be interesting to investigate whether the hydrophobic effect plays a contributory role in the interaction of cell surface polysaccharides.

Acknowledgment. We are grateful to Drs. A. Surolia, Uday Maitra, and V. S. R. Rao, of the Indian Institute of Science Bangalore, R. Nagaraj, of this Center, and E. D. T. Atkins, of the University of Bristol, for help and suggestions. We thank Miss Shreeta for advice and help with calculations and Mr. P. Guptasarma of this Center for experimental advice and help D.B. thanks the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, of which he is an honorary professor.

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Mono- and Di-μ-hydrido-Bridged Carbodications in Acyclic Systems

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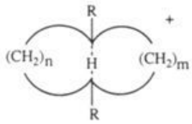
Contribution from the Department of Chemistry, The University of Calgary, Calgary, Alberta T2N 1N4, Canada. *Received August 3, 1992*

Abstract: μ-Hydrido-bridging in carbocations $(\gt C\text{---}H\text{---}C\lt)^+$ involves a two-electron three-center bond. Such structures have previously been observed only when the two carbons are part of a medium ring (monocyclic, bicyclic, or tricyclic frameworks). Using appropriately constructed carbodications, acyclic systems are now shown to form such structures, including a novel example containing two μ-hydrido-bridged units.

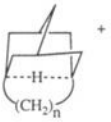
Observable μ-hydrido-bridged solution carbocations have been previously prepared using monocyclic **1**,[1-7] bicyclic **2**,[8-10] and tricyclic **3**[11] ring systems. The existence of monocyclic (medium



1

R=H or alkyl
n = 3,4,5,6
m =3,4,5

2



3 n=5,6

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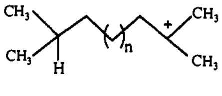
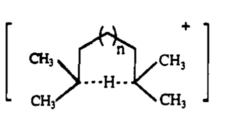


4a n=1

4b n=2



5a n=1

5b n=2

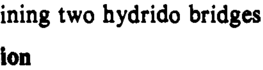
ring) μ-hydrido-bridged cations as solvolysis intermediates is also well established.[12,13] However, in acyclic systems such as **4**, no such bridging exists in the ground-state structure of these cations, although a higher energy intermediate with such a structure (e.g. **5**) is possibly involved in the rapid 1,5- (or 1,6-) hydride transfer seen in these and related cations.[14-18]

We have now found that the expedient of preparing dications, in appropriately constructed organic systems, leads to acyclic μ-hydrido-bridged structures, including the first example of a carbodication containing two hydrido bridges.

Results and Discussion

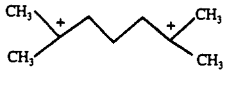
μ-Hydrido-bridged cations can be characterized by the very high field ^{1}H NMR signal of the bridging hydrogen; values from δ −3.5 to −7.9 ppm have been reported (see refs 1–11). However, because of very rapid 1,5- or 1,6-hydride shifts, non-bridged cations such as **4a** can exhibit averaged ^{1}H and ^{13}C NMR peak positions which are in the main very similar to those expected for a μ-H-bridged cation, *with the sole exception of the peak for the migrating hydride*. In **4a**, this peak is found[19] at δ 1.648, i.e. a normal position for the methine proton of an isohexyl group and obviously far removed from the typical bridging hydride position. In this particular case, one can also show from NMR line-broadening studies that **4a** is indeed an equilibrating system.[15,17,18] The same situation applies to cation **4b**,[18] and there are no reported cases where acyclic cation systems are μ-hydrido-bridged structures.

It seems probable that for steric reasons the ground-state conformation of cations **4a** or **4b** is an "extended" chain, i.e. essentially as shown in the formulae. Any hope of observing μ-hydrido bridging in such systems therefore rests on making modifications to **4** which might destabilize this "extended" conformation. In 1985, Siehl and Walter reported[16] the synthesis of cation **6**, where one might hope that the *gem*-dimethyl group would favor a cyclic μ-H-bridged structure (the Thorpe–Ingold effect[20]). However, like **4a**, this cation is also an equilibrating system showing no signs of μ-H bridging (ΔG^{*} for the 1,5-hydride shift = 5.2 ± 0.15 kcal/mol at −122 °C).

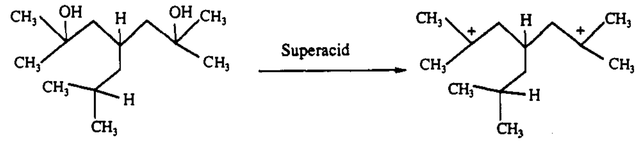


6

2,6-Dimethyl-4-isobutylheptane-2,6-diyl Dication (8). Dication **7** is a known species.[21] Because of charge repulsion one expects such dications to keep the charged atoms maximally apart, i.e. to strongly adopt an "extended" conformation. We therefore thought to prepare a dication of the **7** type, but with an isobutyl group in position 4, i.e. cation **8**. This cation contains structural elements of both the **4a** and **7** structures, but it is obvious that one cannot simultaneously have "extended" substructures representative of both **4a** and **7**.



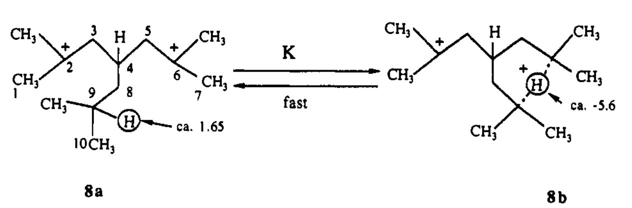
7



9 8

A priori, it seemed probable that the "extended" dication conformation would win out. This then places the isobutyl group of **8** in a conformation where μ-hydrido bridging would seem to be much more favorable. Diol **9** and the related diols **11** and **13** (see later) were prepared using standard procedures developed by McElvain[22] and Bruice[23] for preparing substituted glutaric acids.

Cation **8** was quite cleanly produced by the careful addition of small amounts (generally 5 mg or less) of diol **9** in CD_2Cl_2 to a solution of 1:1 FSO_3H-SbF_5 in SO_2ClF. One immediately notices that the carbodication so produced has a single (area one) high-field ^{1}H NMR signal. However, this signal is not at as high field as the reported μ-H structures, and the position is very temperature dependent, varying from δ −0.78 at 203 K to −1.34 at 159 K.[24] Such temperature effects are characteristic of a nondegenerate rapidly equilibrating system, and the results for **8** can be rationalized as the rapid equilibrium of a μ-H-bridged structure **8b** and an unbridged one **8a**. However, the shift of this high-field "averaged" ^{1}H peak with decreasing temperature is to even higher field. Assuming that **8a** has a δ value of ca. 1.65 for this hydrogen, and that for **8b** it is perhaps δ ca. −5.6,[25] this means that more **8b** is present in the equilibrium mixture as one lowers the temperature (K varies from ca. 0.50 to ca. 0.76). Therefore, from the van't Hoff equation, **8b** must be the slightly *more stable* species in enthalpy terms, with entropy favoring **8a**.[26]



8a 8b

The ^{1}H and some ^{13}C peaks for cation **8** are reported in Table I. There is complete equilibration of all methylene protons and only one signal is seen for all of the methyl groups. These "averaged" signals stay unbroadened even at the lowest temperatures used, indicating therefore that the **8a** ⇄ **8b** equilibration

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(19) Cation **4a** was originally reported by Saunders and Stofko.[14] The published 100-MHz ^{1}H NMR spectrum shows an "averaged" structure based on single peaks being observed for all four CH_3 groups and the α–γ CH_2's. The methine proton was not explicitly located, partly because the ion formation is not completely clean. Therefore, with the discovery of μ-H-bridged cation structures in 1978, it was not entirely clear whether the ion was a rapidly equilibrating system (rapid 1,5-hydride shift) or whether it could be a static μ-H-bridged structure (the high field plot range for the ^{1}H NMR spectrum is shown as ca. δ 0.8 in CW mode, which would have "missed" a possible very high field μ-H). Therefore, in 1978, we measured the ^{13}C NMR spectrum of this cation (reported in Ref. 15), and from this it was clear that the ion must be an equilibrating system (rapid 1,5-hydride shift) since dynamic line-broadening was observed for the averaged α,γ-CH_2 peak and for the averaged methyl peak. In fact, the $C^+ - C{-}H$ averaged peak was broadened into the baseline noise and not even observable. Subsequently, Saunders and Siehl[16-18] have reported similar results. Since we wished to locate the methine proton in ion **4a** for reference purposes, we have re-measured the ^{1}H NMR data for **4a** (400 MHz). The methine signal was easily located from a ^{1}H COSY spectrum (strong coupling to the CH_3 protons). At 400 MHz, one can also cool the solution of **4a** to the extent that one can see ^{1}H NMR line-broadening of the "averaged" methyl signal, from which one can extract rate constants (simulation of data) for the 1,5-hydride shift, k = ca. 3×10^4 s^{-1} at 153 K and ca. 7×10^3 s^{-1} at 145 K, giving a ΔG^{*} for the process of ca. 5.7 kcal/mol. Reference 18 reports a value of 5.2 kcal/mol, while ref 17 gives 4.9 kcal/mol.

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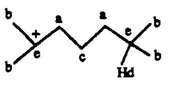
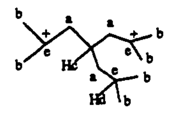
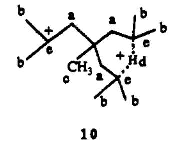
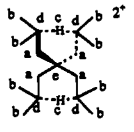
(24) Somewhat variable chemical shifts for the μ-H hydrogen were seen in different samples of this cation prepared under ostensibly similar conditions.

(25) This value is reported[3] for the μ-H hydrogen in the 1,5-dimethylcyclodecyl cation, which should serve as a reasonable model for **8b**.

(26) Using these data in a quantitative way, one obtains $\Delta\Delta H = -6.2 \times 10^2$ cal/mol, $\Delta\Delta G = 9 \times 10^2$ cal/mol, and $\Delta\Delta S = 4$ eu.

Table I. ^{1}H and ^{13}C NMR Parameters for Cations **4a**, **8**, **10**, and **12**

cation	^{1}H shifts (δ ppm)	^{13}C shifts (δ ppm)
 **4a**	(a) 2.73 (4 H) (b) 2.33 (6 H) (c) 1.95 (2 H) (d) 1.65 (1 H) (e) –	50.9 33.8 26.5 *a*
 **8**	(a) 3.20 (6 H) (b) 2.88 (18 H) (c) ca. 2.88 (1 H)[b] (d) –0.78 (1 H) at 203 K (e) –	55.3 36.4 39.1[c] – *a*
 **10**	(a) 3.14 (6 H) (b) 2.87 (18 H) (c) *d* (d) –3.82 (1 H) at 179 K (e) –	58.7[c] 37.9[e] *d* – *a*
 **12**	(a) 2.53 (8 H) (b) 2.23 (24 H) (c) –4.89 (2 H) at 180 K (d) – (e) –	50.5 29.5 (J = 130 Hz) – 160.1 (t, J = 20 Hz) 45.8[c]

[a] Too broad to observe at the S/N level employed. [b] Obscured by the methyl signal. [c] Tentative assignment. [d] Not assigned because impurity peaks dominate in the region expected for this peak. [e] Confirmed from selective ^{1}H decoupling.

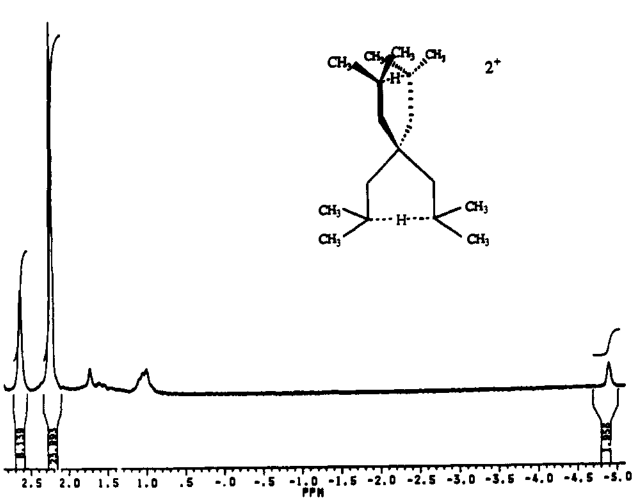
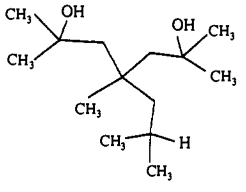


Figure 1. 400-MHz ^{1}H NMR spectrum of cation **12** at 180 K.

process and processes leading to degenerate sets of **8a** and **8b** structures are all rapid. However, the "averaged" signal for carbons 2, 6, and 9 does not show up, presumably because of some broadening.[27] Peaks for the "averaged" ^{13}C methylene and methyl signals are observable.

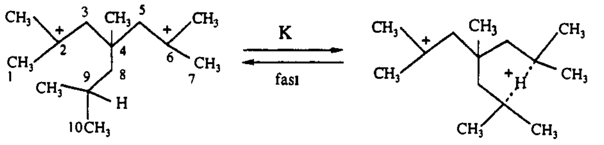
2,4,6-Trimethyl-4-isobutylheptane-2,6-diyl Dication (10). On the basis of the Thorpe–Ingold effect,[20] one should be able to further favor a cyclic structure by replacing the 4-H in **8** with a 4-CH_3 substituent.

Addition of the diol **11** to 1:1 FSO_3H–SbF_5 in SO_2ClF at ca. −116 °C led to a homogeneous mixture with a rather complex ^{1}H NMR spectrum. There was, however, a high-field peak in the δ ca. −4 region, which could be correlated with an "averaged" methyl signal at δ 2.87 by means of a 2D ^{1}H COSY experiment. These two peaks had measured area ratios of 0.96:18, close to the theoretical 1:18 ratio for cation **10** (rapid "averaging"). One can further show that this "averaged" methyl peak is coupled to an "averaged" CH_2 peak (area 6) at δ 3.14. The 4-CH_3 peak of **10** could not be identified with certainty because it does not couple with the rest of the molecule and falls in a region dominated by peaks from "impurity" species. In the best cases, cation **10** formed about 25% of the total ^{1}H signal area.[28] However, at 400 MHz, the region from δ 2.7 to 3.6 (containing the two important peaks of **10**, besides the μ-H signal) is free from interfering impurity peaks so that one can be quite confident about the assignments (listed in Table I).[29] Cooling the solution of **10** to 164 K somewhat broadens both "averaged" CH_2 and CH_3 ^{1}H peaks, an indication that the exchange processes involved have somewhat slower rates than for **8**. As with **8**, no "averaged" ^{13}C peak for carbons 2, 6, and 9 was visible at 180 K.



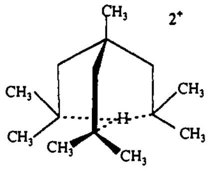
11

The high-field peak observed for **10** has an even greater temperature-dependent chemical shift variation than does the μ-H proton in **8**, varying from δ −3.36 at 200 K to −4.73 at 153 K. One can interpret these data in the same way as was done for **8**, i.e. an equilibration of μ-H-bridged **10b** and unbridged **10a** structures (K varies from ca. 2.2 to 7.3, 200 → 153 K). Both $\Delta\Delta G$ and $\Delta\Delta H$ favor the bridged structure **10b** over **10a**, and the increased temperature dependence seen here is consistent with a larger −*ve* $\Delta\Delta H$ value for **10b** compared to **8b**.



10a **10b**

At this point one should comment on the possibility that a dication such as **10** might form a triply-hydrido-bridged dication structure, i.e. **10c**. Such a species would be expected to have a *very* high field ^{1}H NMR peak for the bridging hydrogen, so that only modest amounts of **10c** in equilibrium with unbridged structures might still have an averaged signal which was high field.



10c

Structure **10c** is perfectly feasible from a molecular orbital picture since the all-in-phase HOMO orbital is the only occupied level. However, high-level (6-31G** at the MP2 level) ab initio molecular orbital calculations[30] show no stability for model structures containing this type of bond. Such structures are

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[27] These solutions were very weak for ^{13}C NMR measurements and hence the S/N ratio was low. From standard NMR line-broadening theory, one expects the most broadening from "averaged" peaks which arise from the rapid chemical exchange of carbons which have a large chemical shift difference in the individual "frozen-out" structures.

[28] Attempts were made to convert the diol **11** into a dichloride, which might have been expected to ionize somewhat more cleanly using SbF_5/SO_2ClF. However, all attempts failed and the major product in each case appeared, from the ^{1}H and ^{13}C NMR data, to be the tetrahydropyran cyclic ether.

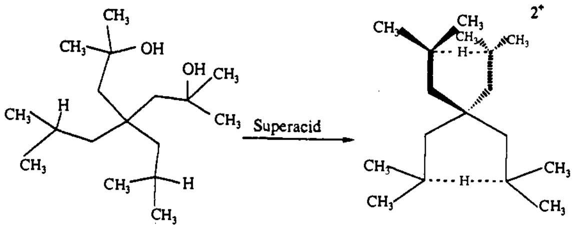
[29] A ^{1}H NMR spectrum of **10** is available as supplementary material.

[30] Unpublished results from Dr. A. Rauk. The model systems used were

calculated to be endothermic by >100 kcal/mol relative to the two separated monocation species (an alkyl carbocation and a μ-H-bridged cation). The possibility still exists that a constrained molecular framework would allow one to prepare such dications; a similar situation exists with regard to the known pagodane[31] and dehydroadamantyl[32] dication systems.

4,4-Diisobutyl-2,6-dimethylheptane-2,6-diyl Dication (12). Replacing the 4-CH_3 group of cation **10** with an isobutyl group now offers the opportunity for *both* charged parts of the molecule to enter into μ-hydrido bridging, while still maintaining maximum charge separation.

Cation **12** was prepared from the corresponding diol **13**, and in contrast to cation **10**, it was quite cleanly produced. It was also thermally more stable than either **8** or **10**. Cation **12**, like the others, has a single quite high field ^1H NMR peak (see Figure 1), in this case of area two. This cation was therefore assigned the di-μ-hydrido-bridged structure **12b**.



13

12b

The ^1H NMR spectrum of **12** shows only three peaks, area ratio 8:24:2. The position for the "averaged" CH_2 and CH_3 peaks (see Table I) is upfield from those of cations **8** and **10**, as would be expected. The ^{13}C NMR spectrum (Table I) shows peaks for the "averaged" methyl and methylene carbons and, in contrast to **8** and **10**, one also sees the carbon peak involved in the di-μ-hydrido bridging.

Cation structure **12b** would be expected to have average D_{2d} symmetry, in which case the above NMR equivalences would necessarily follow. We thought initially that the cation might have a relatively static structure, but a determination of the ^{13}C–^1H coupling constants for the low-field 2 × $(>C{-}{-}{-}H{-}{-}{-}C<)^+$ carbon peak showed otherwise. In a static structure for **12b**, one would expect a doublet for this carbon peak (single ^1H coupling), with an anomolously low coupling constant of ca. 35–40 Hz.[33] The actual coupled ^{13}C–^1H spectrum of **12b** shows a poorly resolved peak for the 2 × $(>C{-}{-}{-}H{-}{-}{-}C<)^+$ carbon, but with selective ^1H decoupling of the CH_3 proton peak, one gets a fairly clean *triplet* for this carbon, J = ca. 20 Hz. This can only mean that the two hydridic hydrogens, already equivalent by symmetry, are in addition undergoing very rapid mutual exchange, presumably by way of a small concentration of nonbridged (open) cation species. There is actually some temperature dependence of the 2 × (μ-H) peak, varying from δ −4.53 at 200 K to δ −5.10 at 160 K, which would be in agreement with this postulate (see previous discussion on cations **8** and **10**). Overall, however, the formally acyclic cation **12** appears to exist almost completely as a double μ-hydrido-bridged system (**12b**), and this is the first example of a cation with such a structure.

Experimental Section

All melting points and boiling points are uncorrected. NMR spectra were obtained on either a Bruker ACE-200 or AM-400 (δ values, J in Hertz) instrument. In descriptions of the ^1H NMR spectra, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet. For ^{13}C NMR, s = quaternary, d = CH, t = CH_2, and q = CH_3. Carbon multiplicities were determined using DEPT 90 and 135 sequences. Specific assignments were usually based on 2D HETCOR and COSY spectra. Unless noted, $CDCl_3$ was used as the NMR solvent. Mass spectra were determined on a VG-7070 or Kratos MS-80 instrument. Low-resolution GC-MS was performed on a Hewlett-Packard Model 5890 chromatograph coupled to a HP 5971A EI mass spectrometer, using a 12.5 m × 0.20 mm (i.d.) DB-1 capillary column. Thin layer chromatography (TLC) was performed on precoated silica gel 60 F_{254} plates (Merck 5554).

Ethyl 2-cyano-5-methylhex-2-enoate was prepared in 71% yield using the general method of Cope,[35] bp ca. 50–70 °C (0.1 mm) [lit.[36] 82 °C/4 mm].

2,4-Dicyano-3-isobutylglutarimide was prepared from the above compound in 60% yield using the general method of McElvain[22] as a crystalline material (recrystallization from ethyl acetate) but the ^1H NMR spectrum in 2:1 (v/v) $CDCl_3$–CD_3OD indicates a mixture of isomers. Anal. Calcd for $C_{11}H_{13}N_3O_2$: C, 60.26; H, 5.60; N, 19.17. Found: C, 60.55; H, 6.02; N, 18.96. MS: 204 (10), 177 (18), 137 (55), 110 (28), 67 (58), 43 (100).

3-Isobutylglutaric Acid. The above imide was hydrolyzed at reflex with 70% (v/v) H_2SO_4 to give a 42% yield of recrystallized (ethyl acetate–hexane) title compound, mp 40–42 °C. Anal. Calcd for $C_9H_{10}O_4$: C, 57.43; H, 8.57. Found: C, 57.71; H, 8.69. ^1H NMR: 2.0–2.6 (5 H, complex), 1.65 (1 H, heptet, J = 6.5), 1.22 (2 H, d of d, J = 7 and 7), 0.94 (6 H, d, J = 6.5). ^{13}C NMR: 179.5 (2 × s), 43.8 (t), 38.9 (2 × t), 29.8 (d), 25.1 (d), 22.5 (2 × q). MS: 187 (3), 171 (4), 155 (8), 129 (15), 111 (60), 28 (100).

Dimethyl 3-Isobutylglutarate. The acid (2.5 g, 13.3 mmol), trimethylsilyl chloride (10 mL) in 50 mL of dry methanol was stirred for 12 h to give 2.6 g (90%) of colorless liquid after distillation; bp 60 °C (0.1 mm). Anal. HRMS Calcd for $C_{11}H_{20}O_4$: M^+ − 15, 201.1127, M^+ − 31, 185.1177. Found: 201.1147 and 185.1182. ^1H NMR: 3.65 (6 H, s), 2.3–2.5 (5 H, complex multiplet), 1.60 (1 H, heptet, J = 6.75), 1.18 (2 H, d of d, J = 6.8 and 6.8), 0.88 (6 H, d, J = 6.75). ^{13}C NMR: 171.5 (2 × s), 51.4 (q), 43.2 (t), 38.2 (2 × t), 29.6 (d), 24.9 (d), 22.2 (2 × q).

2,6-Dimethyl-4-isobutylheptane-2,6-diol (9). The above ester (200 mg, 0.93 mmol) in 2 mL of dry THF was added to methyl lithium (4 mL, 1.5 M in ether, 6 mmol) at −78 °C with stirring and under an N_2 atmosphere. After 10 h at room temperature, workup and flash chromatography using hexane–ethyl acetate (3:1) gave 116.8 mg of the solid diol (56%), recrystallized from methylene chloride, mp 80–82 °C. Anal. Calcd for $C_{13}H_{28}O_2$: C, 72.17; H, 13.04. Found: C, 72.43; H, 13.25. ^1H NMR: 1.91 (1 H, m, H 4), 1.67 (2 H, d of d, J = 6.0 and 14.4, H 3,5), 1.58 (1 H, heptet, J = 6.6, CH of isobutyl), 1.38 (2 H, d of d, J = 3.5 and 14.4, H 3,5), 1.25 (6 H, s), 1.24 (6 H, s), 1.16 (2 H, d of d, J = 7.0 and 7.0, CH_2 of isobutyl), 0.91 (6 H, d, J = 6.6). ^{13}C NMR: 71.8 (2 × s, C2–C6), 49.5 (2 × t, C3–C5), 49.4 (t, CH_2 of isobutyl), 32.3 (2 × q, diastereomeric CH_3), 28.2 (2 × q, diastereomeric CH_3), 26.6 (d, C4), 25.9 (d, CH of isobutyl), 22.9 (2 × q, CH_3 of isobutyl). MS: 201 (2), 169 (8), 140 (18), 69 (44), 59 (100).

Ethyl 2-cyano-3,5-dimethylhex-2-enoate was prepared in 73% yield using the method of Cope,[35] bp 94 °C (0.08 mm) [lit.[35] 130–133 °C (12 mm)]. From ^1H and ^{13}C NMR, the material is a 2:3 mixture of geometric isomers.

2,4-Dicyano-3-isobutyl-3-methylglutarimide was prepared by the general method of McElvain[22] in 59% recrystallized yield, mp 235–237 °C. Anal. Calcd for $C_{12}H_{15}N_3O_2$: C, 61.79; H, 6.48; N, 18.01. Found: C, 61.99; H, 6.46; N, 17.90. MS: 233 (2), 218 (8), 191 (31), 151 (82), 108 (33), 81 (48), 43 (100). Although the crystalline compound may be a single stereoisomer, the ^1H and ^{13}C NMR spectra indicated a mixture of stereoisomers present in solution.

3-Isobutyl-3-methylglutaric Acid. The above imide was hydrolyzed in refluxing 70% (v/v) aqueous sulfuric acid (30 g in 250 mL) for 18 h. After workup and recrystallization from ethyl acetate–hexane, there was obtained 21.9 g (84%) of the title acid, mp 60–62 °C. Anal. Calcd for $C_{10}H_{18}O_4$: C, 58.38; H, 8.97. Found: C, 59.56; H, 8.97. ^1H NMR: 2.59 and 2.54 (4 H, J_{gem} = 15.3), 1.73 (1 H, m), 1.41 (2 H, d, J = 5.3), 1.65 (3 H, s), 0.96 (6 H, d, J = 6.75). ^{13}C NMR: 178.0 (2 × s), 48.8 (t), 43.0 (2 × t), 35.6 (s), 25.3 (q), 25.2 (2 × q), 23.7 (d). MS: 185 (8), 169 (15), 156 (13), 143 (54), 127 (51), 125 (63), and 83 (100).

Dimethyl 3-Isobutyl-3-methylglutarate. To the above acid (19.5 g, 96.5 mmol) in 250 mL of dry methanol was added trimethylsilyl chloride (50 mL). After the mixture was stirred at room temperature for 12 h, workup and distillation, bp 73 °C (0.1 mm) gave 18.1 g (82%) of the title ester. Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 61.70; H, 9.57. HRMS Calcd for $C_{12}H_{22}O_4$: M^+ − 31, 199.1334. Found:

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199.1309. ^{1}H NMR: 4.81 (6 H, s), 2.50 and 2.46 (4 H, J_{gem} = 15.3), 1.70 (1 H, m), 1.36 (2 H, d, J = 5.3), 1.11 (3 H, s), 0.93 (6 H, d, J = 6.6). ^{13}C NMR: 172.3 (2 × s), 51.1 (2 × q), 48.7 (t), 43.1 (2 × t), 35.8 (s), 25.30 (q), 25.26 (2 × q), 23.7 (d). MS: 199 (35), 157 (82), 141 (49), 125 (82), 83 (100).

4-Isobutyl-2,4,6-trimethylheptane-2,6-diol (11). The above ester (0.50 g, 2.17 mmol) in 2 mL of THF was added to methylmagnesium chloride (7.75 mL, 2.8 mmol/mL) in 15 mL of THF with stirring at 0 °C. After 1 h, the temperature was raised to reflux for 4 h. Workup (ether extractions) and flash chromatography separation on silica gel (4:1 hexane–ethyl acetate) yielded 178 mg (35%) of the title diol, mp 85–87 °C (methanol). Anal. Calcd for $C_{14}H_{30}O_2$: C, 72.98; H, 13.13. Found: C, 72.94; H, 13.32. ^{1}H NMR: 3.07 (2 H, b s, OH), 1.78 and 1.76 (4 H, both d, J_{gem} = 15.3, H 3,5), 1.66 (1 H, m, CH of isobutyl), 1.38 (2 H, d, J = 5.0, CH_2 of isobutyl), 1.30 and 1.29 (12 H, both s), 1.11 (3 H, s, 4-CH_3), 0.93 (6 H, d, J = 6.6). ^{13}C NMR: 72.0 (2 × s), 54.1 (t, CH_2 of isobutyl), 50.0 (2 × t, C3–C5), 36.6 (s, C4), 33.0 and 32.9 (both 2 × q, diastereotopic CH_3), 26.8 (q, 4-CH_3), 25.9 (2 × q, CH_3 of isobutyl), 24.0 (d, CH of isobutyl). MS: 215 (1), 197 (6), 179 (3), 154 (8), 139 (8), 98 (29), 83 (58), 59 (100).

Ethyl 2-cyano-3-isobutyl-5-methylhex-2-enoate was prepared in 68% yield as described by Cope,[35] bp 93–94 °C (0.1 mm) [lit.[35] 116–118 °C (3 mm)]. ^{1}H NMR (400 MHz): 4.26 (2 H, q, J = 7.0), 2.72 (2 H, d, J = 7.0), 2.47 (2 H, d, J = 7.0), 2.00 (1 H, heptet, J = 7.0), 1.91 (1 H, heptet, J = 7.0), 1.33 (3 H, t, J = 7.0), 0.98 (6 H, d, J = 7.0), 0.89 (6 H, d, J = 7.0). ^{13}C NMR: 179.4 (s), 161.4 (s), 115.6 (s), 105.7 (s), 61.2 (t), 46.7 (t), 40.9 (t), 26.5 (d), 26.0 (d), 22.1 (2 × q), 22.0 (2 × q), 13.6 (q).

2,4-Dicyano-3,3-diisobutylglutarimide was prepared from the above compound in 82% yield using the general method of McElvain[22] to give a white solid (ethanol–water), mp 207–209 °C. Anal. Calcd for $C_{15}H_{21}N_3O_2$: C, 65.43; H, 7.69; N, 15.26. Found: C, 65.68; H, 7.40; N, 15.01. ^{1}H NMR (isomers): 4.78 (2 H, s), 2.16 (1 H, m), 2.0–1.8 (3 H, complex), 1.67 (2 H, d, J = 5.0), 1.17 (6 H, d, J = 5.9), 1.07 (6 H, d, J = 6.8). ^{13}C NMR (CD_3OD) (isomers): 165.4 (s), 114.4 (s), 46.0 (t), 45.5 (t), 43.7 (s), 25.6 (q), 25.4 (q), 23.9 (d), 23.6 (d). MS: 274 (2), 260 (90), 218 (65), 193 (70), 176 (90), 151 (100).

3,3-Diisobutylglutaric Acid. The above imide was hydrolyzed with 70% H_2SO_4 (23.3 g, 95.5 mmol, 200 mL) at reflux for 24 h to give, after workup, 14.5 g (70%) of the title acid, mp 82–84 °C (ethyl acetate). Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.90; H, 9.90. Found: C, 63.98; H, 9.66. ^{1}H NMR: 2.61 (4 H, s), 1.70 (2 H, m), 1.50 (4 H, d, J = 5.3), 0.94 (12 H, d, J = 6.7). ^{13}C NMR: 177.5 (2 × s), 45.4 (2 × t), 40.6 (2 × t), 36.5 (s), 24.6 (4 × q), 23.1 (2 × d). MS: 185 (77), 170 (63), 125 (93), 83 (95), 43 (100).

Dimethyl 3,3-Diisobutylglutarate. Using the same method as was used for preparing the other esters, an 83% yield, bp 108 °C (0.1 mm), of the title ester was obtained. HRMS Calcd for $C_{15}H_{28}O_4$: $M^+ - 31$, 241.1804. Found: 241.1792. ^{1}H NMR: 3.63 (6 H, s), 2.55 (4 H, s), 1.69 (2 H, m), 1.45 (4 H, d, J = 4.3), 0.91 (12 H, d, J = 6.7). ^{13}C NMR: 172.3 (2 × s), 51.0 (2 × q), 45.8 (2 × t), 41.0 (2 × t), 39.0 (s), 25.3 (2 × q), 23.5 (2 × d). MS: 241 (29), 199 (96), 184 (56), 125 (100), 83 (74).

4,4-Diisobutyl-2,6-dimethylheptane-2,6-diol (13). Using the same procedure as described for **11**, a 28% yield of the diol **13** was obtained, mp 132–134 °C (methanol). Anal. Calcd for $C_{17}H_{36}O_2$: C, 74.94; H, 13.32. Found: C, 74.62; H, 13.31. ^{1}H NMR: 3.16 (2 H, OH), 1.82 (4 H, s, H 3,5), 1.67 (2 H, m, CH of isobutyl), 1.52 (4 H, d, J = 4.9, CH_2 of isobutyl), 1.31 (12 H, s), 0.95 (12 H, d, J = 6.6). ^{13}C NMR: 71.9 (2 × s), 48.8 (2 × t, C 3,5), 48.7 (2 × t, CH_2 of isobutyl), 33.3 (4 × q), 25.7 (4 × q, CH_3 of isobutyl), 23.6 (2 × d). MS: 240 (8), 239 (30), 165 (15), 125 (42), 83 (54), 69 (100).

2,6-Dimethyl-2-heptanol. Commercially available 2,6-dimethyl-1-heptene (1.26 g, 10.0 mmol) was added dropwise to mercuric acetate (3.19 g, 10.0 mmol) in a mixture of THF (10 mL) and water (10 mL) with stirring at room temperature. After 20 min, 10 mL of aqueous $NaBH_4$ (0.5 M in 3 M NaOH) was added. After 10 min of stirring the reaction was diluted with saturated NaCl, extracted with ether (3 × 50 mL), and dried, the solvent was evaporated, and the residue was chromatographed on silica gel (4:1 hexane–ethyl acetate) to give 917 mg (64%) of the title alcohol.[37]

Cation Preparations. The appropriate alcohol, usually about 5–10 mg, was dissolved in 50 μL of CD_2Cl_2 solution and then added to a precooled (−117 °C, ethanol slush bath) solution of 1:1 FSO_3H–SbF_5 (Magic acid) in SO_2ClF solvent in a 5 mm NMR tube. The organic solution was added dropwise on the side of the tube above the acid solution and then washed into the acid with a coiled platinum stirrer. All cation spectra were determined at 400 MHz (^{1}H) and 100 MHz (^{13}C) and are referenced to $CHDCl_2$ (δ 5.32) and $^{13}CD_2Cl_2$ (δ 53.8). Most spectra were run in the locked mode (CD_2Cl_2). Temperature calibration was carried out using a reference methanol sample (to 173 K). In the case of dications **8** and **10**, the first spectra recorded contained the cation peaks. For cation **12**, substantial amounts of the diprotonated alcohol were first seen. When the solution is left at 200 K in the spectrometer, the alcohol is slowly transformed into the dication. All three cations decompose at low temperatures, with the *tert*-butyl cation as a prominent feature in the resulting NMR spectra.

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Supplementary Material Available: The 400-MHz ^{1}H NMR spectrum of **10**, showing the "window" region from δ 2.7 to 3.6 ppm (1 page). Ordering information is given on any current masthead page.