Table I. Monosubstituted Dodecahedranes

substituent	mp, °C	^{13}C δ (quart C)	m/z (M^+) calcd	m/z (M^+) obsd
Br	>240	96.98	340.0650	340.0628
Cl	>280	104.39	294.1175	294.1140
F	>260	137.64	278.1487	278.1476
COOH	>250	*b*	304.1463	304.1449
COOMe	192-193	84.54	319[c]	319
CH_2OH	>250	81.86	290.1681	290.1659
CHO	>250	90.00	288.1514	288.1519
$CONH_2$	>250	85.61	303.1623	303.1640
C_6H_5	200-201	84.42	336.1870	336.1874
$OCOCF_3$	183-185[a]	126.47	258.1408[d]	258.1407
OH	>250	115.99	276.1515	276.1482
ONO_2	220	129.89	259[e]	259
$NHCOCH_3$	>250	95.77	317.1780	317.1772

[a] Dec 220 °C. [b] Very low solubility. [c] CI (M + 1). [d] (M^+ - CF_3COOH). [e] (M^+ - ONO_2).

in hot acetonitrile and subsequent hydration delivered **6** (100%).

Acknowledgment. We are grateful to the National Institutes of Health for their generous financial support of this research program (Grant AI-11490).

Chemical Properties of Dodecahedrane. The Dodecahedryl Cation and 1,16-Dodecahedryl Dication. Regioselective Difunctionalization of the Sphere[1a]

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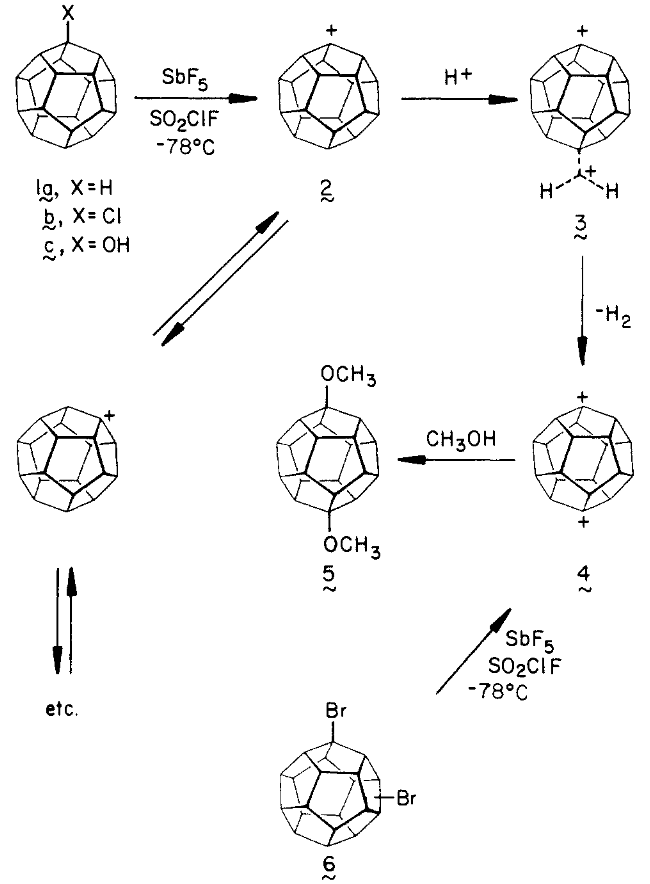
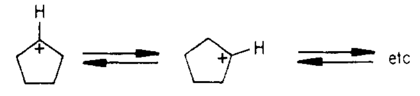
The challenge of defining practical synthetic routes for arrival at dodecahedrane (**1a**) has been met in two laboratories.[2,3] The preceding report defines for the first time various protocols capable of delivering a wide range of monofunctionalized dodecahedranes.[4] Practical exploitation of this chemistry rests heavily, although not exclusively, on *transient generation and efficient trapping* of the monocation. Several empirical observations made in the course of these studies implicated for $C_{20}H_{19}^+$ (**2**) a lability that was not at all expected.[5] For this reason, we sought to generate and examine **2** under long-life conditions. Herein is described the direct spectral observation of **2** in superacid solution, an analysis of its stability and capacity for degenerate isomerization, and the remarkable ease of its conversion to the 1,16-dication **4**.

Careful dissolution of 5 mg of chlorododecahedrane (**1b**)[4] in 1 mL of SO_2ClF containing ~250 mg of SbF_5 at -78 °C in a 5-mm NMR tube gave a pale yellow-colored solution. The 200 MHz ^1H NMR spectrum[6a] of this solution at -70 °C revealed a set of three absorptions at δ 4.64 (br, 3 H), 3.05 (br, 7 H), and 2.59 (br, 9 H) as seen in Figure 1A.[6b] The peaks did not split further at 500 MHz. The 50 MHz ^{13}C spectrum consisted of six absorptions at 363.9 (s), 81.1 (d), 64.4 (d), 64.1 (d), 63.0 (d), and 60.9 (d) ppm, clearly indicating formation of the static dodecahedryl cation (**2**). Ion **2** was similarly obtained from dodecahedranol (**1c**),[4] although more slowly. The limited solubility of dodecahedrane necessitated that the superacidic medium be warmed to 0 °C for dissolution to occur. Under these conditions, smooth conversion to **2** also materialized.



We considered that the dodecahedryl cation could undergo rapid hydrogen scrambling (through 1,2-hydride shifts) similar to that observed in cyclopentenyl cation **7**, a process that would render



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all the carbon and hydrogen atoms equivalent. However, no such degenerate process was observed as indicated by the lack of change in the ^1H NMR line shapes, even when solutions of **2** were allowed to warm to 0 °C. Thus, the lower barrier for such degenerate rearrangement is approximately 15 kcal/mol. The findings presented below suggest that the actual barrier is not apt to be much higher however.

Upon standing in the superacidic solution for 6-7 h at -50 °C, monocation **2** is slowly and irreversibly transformed into a new species displaying much simplified NMR spectra. Only two absorptions are seen at δ 4.74 (br, 6 H) and 3.23 (br, 12 H) in

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(1) (a) Considered as Stable Carbocations, Part 271 at the University of Southern California. (b) The Ohio State University Postdoctoral Fellow, 1986-1988.

(2) (a) Ternansky, R. J.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4503. (b) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Kentgen, G. *Ibid.* **1983**, *104*, 5446.

(3) Fessner, W.-D.; Murty, B. A. R. C.; Worth, J.; Hunkler, D.; Fritz, H.; Prinzbach, H.; Roth, W. D.; Schleyer, P. v. R.; McEwen, A. B.; Maier, W. F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 452.

(4) Paquette, L. A.; Weber, J. C.; Kobayashi, T., preceding paper in this issue.

(5) Unpublished observations of J. C. Weber and T. Kobayashi at The Ohio State University.

(6) (a) The NMR spectra were recorded on a Varian Associates Model VXR-200 NMR spectrometer equipped with a variable temperature broad band probe. (b) The observed relative intergral area of the three absorptions of 3:7:9 in **2** indicates that the apical hydrogen atom at the 16-position which is farthest from the positive charge experiences more deshielding (δ = 3.05) than the other belt hydrogens (δ = 2.59) which are much closer to the positive charge. This may be due to a unique cage effect in the dodecahedrane skeleton.

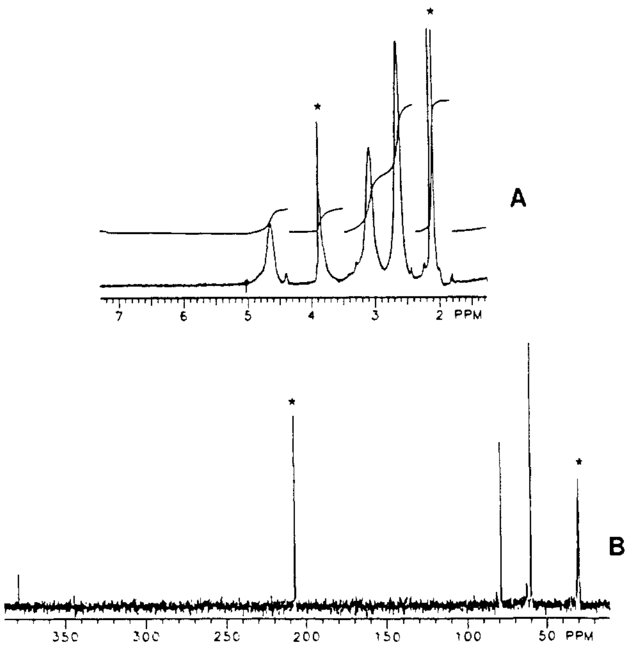
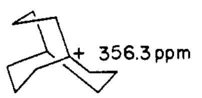


Figure 1. (A) ^{1}H spectrum (200 MHz) of 1-dodecahedryl cation **2** in SbF_2/SO_2ClF at -70 °C. (B) Proton decoupled ^{13}C NMR spectrum (50 MHz) of 1,16-dodecahedryl dicaton **4** in SbF_5/SO_2ClF at -70 °C. * peaks due to lock solvent (acetone-d_6 containing some water).

the ^{1}H spectrum at -70 °C. The three signals at 379.2 (s), 78.8 (d), and 59.8 (d) ppm that constitute the ^{13}C spectrum are illustrated in Figure 1B.

These data allow the new species to be assigned as the symmetrical apical/apical 1,16-dodecahedryl dication (**4**). The formation of this unique species can be rationalized by protolytic ionization[7] of the C-H bond at position 16[8] involving an intermediate cation such as **3**. Independent generation of **4** was accomplished by ionization of the isomeric mixture of dibromododecahedranes (**6**) which is produced when **1** is brominated in the presence of $AlBr_3$. This mixture is constituted of three $C_{20}H_{18}Br_2$ components (GC-MS analysis) in the ratio of 5:6:2 with the minor constituent being **11**. Since the only observable dication is **4**, 1,2-hydride shifts clearly occur readily once the system is charged.

The ^{13}C chemical shifts of the positively charged centers in **2** (363.9 ppm) and **4** (379.2 ppm) happen to be the most deshielded ever observed for carbocationic species. Those previously recorded at the limit of the deshielding range include the 1-bicyclo[3.3.3]undecyl cation (**8**) and the 1,5-bicyclo[3.3.3]undecyldiyl dication (**9**).[9] Application of the ^{13}C chemical shift additivity criterion[10] reveals a net ^{13}C chemical shift deshielding of 283 ppm for **2** and 610 ppm for **4** in accord with the progession from mono- to dication. The magnitude of deshielding per unit positive charge in both **2** and **4** is less than that observed in a typical tertiary carbocation such as 1-methyl-1-cyclopentyl cation ($\Sigma\Delta = 374$).[10] This indicates the prevalence of some unique cage shielding effect in the cation whose origin is not yet clear.



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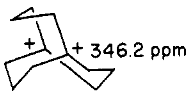

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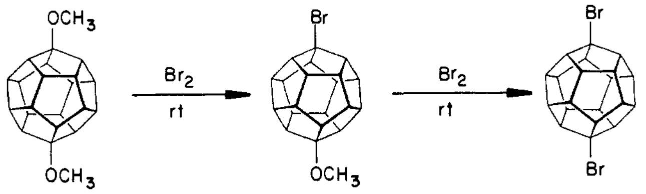
Dication **4** was found to be rather stable at 0 °C for several days. Quenching of solutions of this ion in methanol gave 1,16-dimethoxydodecahedrane (**5**)[11a] in ≥85% yield. When stirred in liquid bromine at room temperature, **5** is slowly transformed into **10**[11b] and ultimately into **11**.[11c] The isomeric purity of these products as determined by capillary GC is 100%. Therefore, the ready preparation of dication **4** makes available the capacity for effective regioselective functionalization of the dodecahedrane framework.



5 10 11

The possibility also exists that monocation **2** and dication **4** can be deprotonated to form dodecahedrene and dodecahedradiene, respectively. These unsaturated molecules may be involved in deprotonative condensation or decomposition processes of the ions and may even prove isolable upon controlled deprotonation with hindered bases. Studies are continuing in this direction.

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(7) Adventitious protic acid is invariably difficult to remove from such media.

(8) The independent conversion of **6** to **4** technically allows for ionization to occur initially at the other available sites. 1,2-Hydride migration would follow so as to position the positive charges as mutually distal as possible.

(9) Olah, G. A.; Liang, G.; Schleyer, P. v. R.; Parker, W.; Watt, C. I. F. *J. Am.* Chem. *Soc.* **1977**, 99, 966.

(10) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683.

(11) (a) **5**: mp 247-248 °C (from hexane-benzene); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.50 (br s, 12 H), 3.42 (br s, 6 H), 3.24 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 122.28, 67.84, 65.51, 51.25; MS *m/z* (M^+) calcd 320.1786, obsd 320.1781. (b) **10**: mp > 270 °C (from hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.95-3.83 (m, 3 H), 3.75-3.35 (m, 15 H), 3.22 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 78.81, 68.10, 65.70, 65.04, 51.27 (two quaternary carbons not observed); MS *m/z* (M^+) calcd 370.0756, obsd 370.0743. (c) **11**: mp > 270 °C (from hexane-benzene, 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.93 (br s, 6 H), 3.60 (br s, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 95.58, 79.09, 65.26; MS *m/z* (M^+) calcd 417.9754, obsd 417.9727.

Cyclopropanation of Spherical Hydrocarbons without Need for Prior Olefination. The Synthesis of Cyclopropadodecahedranes

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Carbocyclic ring systems are recognized to experience considerable structural distortion and concomitant enhancement of ground-state strain when fused to a cyclopropane ring across a key C-C bond. Notable examples include adamantane → 1,3-dehydroadamantane,[3] bicyclo[2.1.0]pentane → [2.1.1]propellane,[4] and bicyclo[1.1.0]butane → [1.1.1]propellane.[5] The synthetic protocol most commonly employed to produce such highly strained

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(1) The Ohio State University Postdoctoral Fellow, 1986-1988.

(2) Author to whom inquiries should be addressed concerning the X-ray crystallographic analysis.

(3) (a) Synthesis: Pincock, R. E.; Torupka, E. J. *J. Am. Chem. Soc.* **1969**, *91*, 4593. (b) Structure: Gibbons, C. S.; Trotter, J. *Can. J. Chem.* **1973**, *51*, 87.

(4) Wiberg, K. B.; Walker, F. H.; Pratt, W. E.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 3638.

(5) (a) Synthesis: Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239. (b) Structure: Honneger, E.; Huber, H.; Heilbronner, E.; Dailey, W. P.; Wiberg, K. B. *Ibid.* **1985**, *107*, 7172. (c) Wiberg, K. B.; Dailey, W. P.; Walker, F. H.; Waddell, S. T.; Crocker, L. S.; Newton, M. *Ibid.* **1985**, *107*, 7247.