

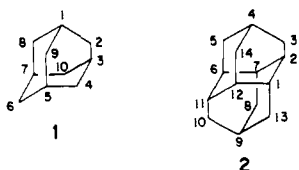
# Bridgehead Adamantyl, Diamantyl, and Related Cations and Dications<sup>1a</sup>

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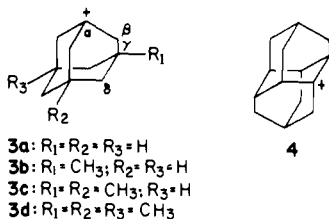
**Abstract:** The bridgehead 1-adamantyl cation **3a** and a series of methyl-substituted adamantyl cations **3b-d** have been prepared in superacid medium and characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The relative deshielding of bridgehead  $\gamma$  carbons with respect to  $\beta$ -methylenes has been rationalized in terms of a C-C hyperconjugative effect. The cation generated from the ionization of *exo*-5,6-trimethylene-2-norbornyl derivatives has been shown to be the equilibrating 2,3-trimethylene-2-norbornyl cation **12**. The temperature-dependent <sup>13</sup>C NMR spectroscopic studies on **12** indicate the barrier for the degenerate *exo*-2,3-hydrogen shift,  $\Delta G^\ddagger = 7.2$  kcal/mol. The cation **12** in a solution of SO<sub>2</sub>ClF is stable even at room temperature; however, in a solution of SO<sub>2</sub>, it smoothly and irreversibly rearranges to bridgehead 1-adamantyl cation **3a**. On the other hand, 2-methyl-5,6-*exo*-trimethylene-2-norbornyl cation **17** was found to be quite stable. The 1-adamantyl cation was also studied as its isolated SbF<sub>6</sub><sup>-</sup> salt by solid-state CP/MAS <sup>13</sup>C NMR spectroscopy. The bridgehead 1- and 4-diamantyl cations **4** and **27** were also prepared and studied. Heteronuclear-correlated 2D NMR spectra were also obtained for **3a** and **4** and used in many assignments of the NMR shifts. Cation **27** slowly and irreversibly rearranges to **4**. The cation **4** was also generated by the ionization of 3-diamantyl derivatives. The above rearrangements to the thermodynamically more stable ion **4** has been rationalized in terms of facile intermolecular hydrogen shifts rather than intramolecular shifts. The bridgehead adamantyl cations **4** and **27** also derive their stability from C-C hyperconjugative effects similar to their adamantyl analogues. In contrast to the instability of secondary 3-diamantyl cation the corresponding 3-methyl- and 3-phenyl-substituted analogues were found to be rather stable. 3,3'-(1,1'-Biadamantyl) dication **6** and 4,9-diamantyl dication **5** were also generated and studied. The C-C hyperconjugative stabilizing interaction which is found "operative" in all of the bridgehead cations including dication **6** is absent in the 4,9-diamantyl dication **5**. Charge-charge repulsion in **5** seems to diminish such C-C hyperconjugative interaction. All attempts to prepare the 1,3-adamantyl dication **8** or the 1,6-diamantyl dication **7** were unsuccessful.

Over the past 2 decades, extensive research has been carried out pertaining to the chemistry of adamantane, diamantane, and other so-called diamondoid molecules.<sup>2,3</sup> The unique structural features of adamantane (**1**) and diamantane (**2**) are also ideal for a systematic study of their cations, relating to both structure and chemical reactivity. The tight interlocking of cyclohexane rings

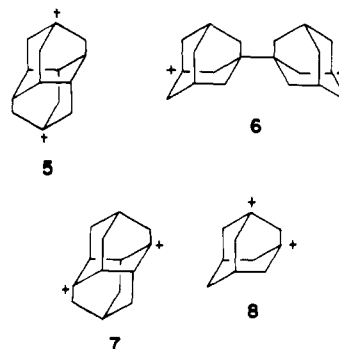


into rigid, relatively strain-free chair conformations allows no easy formation of double bonds and no back-side (electrophilic or nucleophilic) attack.

In our preliminary work, the preparation and study of the 1-adamantyl cation **3a** and the 1-diamantyl cation **4** were reported.



They were characterized by <sup>1</sup>H NMR spectroscopy.<sup>4,5</sup> We now wish to describe in detail the preparation and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic characterization of bridgehead adamantyl, substituted adamantyl, related bridgehead diamantyl, and 3-substituted diamantyl cations. Studies relating to the formation of **3a** from trimethylenenorbornyl derivatives have been included along with the cross-polarization magic angle spinning <sup>13</sup>C NMR spectroscopic study of **3a** in its crystalline state (as its SbF<sub>6</sub><sup>-</sup> salt). The <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts in **3a** and **4** were also cross-correlated by using heteronuclear correlated two-dimensional (2D NMR) spectra. We also describe the preparation and spectroscopic characterization of the related 4,9-diamantyl dication **5**



(congressane dication) and the 3,3'-(1,1'-biadamantyl) dication **6**. Attempted preparation of the 1,6-diamantyl dication **7** and the 1,3-adamantyl dication **8** were, however, unsuccessful.

## Results and Discussion

**1-Adamantyl Cation 3a and Related Methyl-Substituted Cations (3b-d).** The bridgehead 1-adamantyl cation **3a** can be readily prepared by treating adamantane (**1**) with superacids

(1) (a) Stable Carbocations. 258. For part 257, see: Krishnamurthy, V. V.; Iyer, P. S.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* 1984, 106, 7068. (b) University of Southern California. (c) Case Western Reserve University. (d) Visiting Scientist from the University of Szeged, Hungary. (e) Princeton University. (f) Friedrich-Alexander Universität, Erlangen, Nürnberg.

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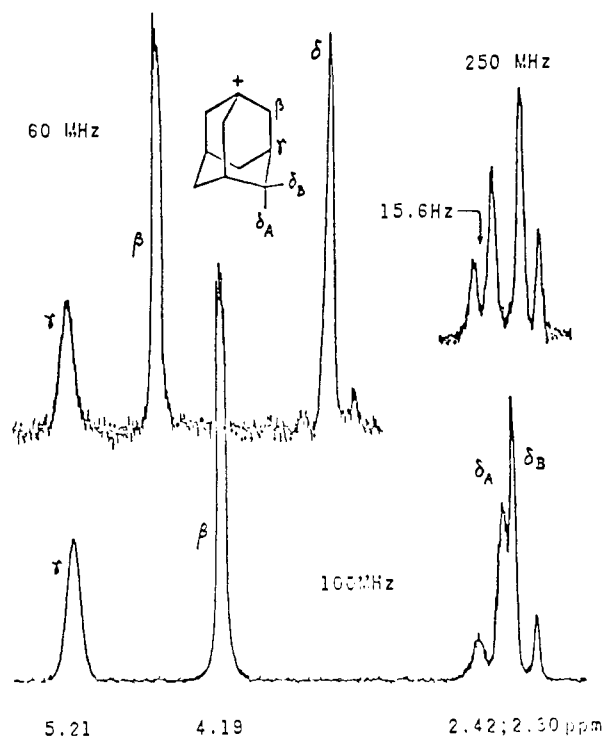
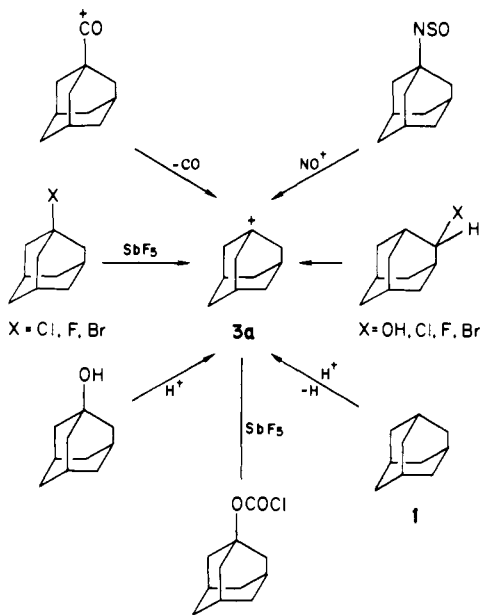


Figure 1.  $^1\text{H}$  NMR spectrum of 1-adamantyl cation **3a** at (a) 14.09 kG (60 MHz), (b) 23.48 kG (100 MHz), and (c) 58.70 kG (250 MHz).

( $\text{FSO}_3\text{H}/\text{SbF}_5$  or  $\text{HF}/\text{SbF}_5$ ) with or without low nucleophilicity solvents ( $\text{SO}_2$  or  $\text{SO}_2\text{ClF}$ ). The ion **3a** can also be generated from a variety of precursors including 1- and 2-substituted adamantanes.<sup>6-8</sup> The mechanism of the rearrangement of the 2-



adamantyl cation formed as an intermediate in the latter case has been discussed earlier.<sup>8,9</sup>

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(9) A rapid intermolecular hydride exchange specifically involving bridgehead hydrogens has been ruled out since no change in the  $^1\text{H}$  NMR spectrum occurred over a temperature range of  $-90$  to  $+120$   $^\circ\text{C}$ . Exceptionally high barriers have been estimated for such a process; see: Vogel, P.; Saunders, M.; Thielecke, W.; Schleyer, P. v. R. *Tetrahedron Lett.* **1971**, *18*, 1429. Also, see: Schleyer, P. v. R.; Lam, L. K. M.; Raber, D. J.; Fry, J. L.; McKervey, M. A.; Alford, G. R.; Cuddy, B. D.; Keizer, V. G.; Geluk, A. W.; Schlatman, J. L. M. A. *J. Am. Chem. Soc.* **1970**, *92*, 5246.

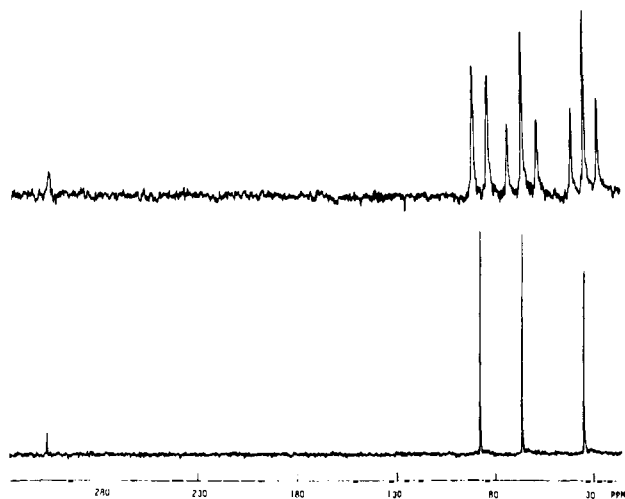
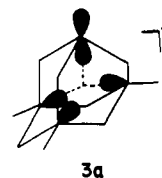


Figure 2.  $^{13}\text{C}$  NMR spectra (20 MHz) of 1-adamantyl cation **3a** in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solution at  $-80$   $^\circ\text{C}$ : (A) proton decoupled; (B) proton coupled.

Of particular interest is the generation of **3a** starting from 2-*exo*-(chloro)hydroxy-*exo*-trimethylenenorbornane in  $\text{SbF}_5/\text{SO}_2$  solution at temperatures above  $-30$   $^\circ\text{C}$  (vide infra).<sup>7</sup>

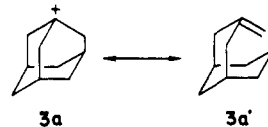
The 60-MHz  $^1\text{H}$  NMR spectrum of the 1-adamantyl cation **3a** (Figure 1) consists of three unresolved multiplets at  $\delta$  2.30 (6 H), 4.19 (6 H) and 5.19 (3 H) (Table I). The relative intensities of the signals require assignment of the lowest field peak to the  $\gamma$  (bridgehead) protons. This indicates that  $\beta$  protons which are nearest to the (formal) positive charge are not as deshielded as the  $\gamma$  protons. A better resolved spectrum is obtained at 100 MHz, wherein the  $\delta$  protons are observed as an AB pattern. At 250 MHz, this AB pattern is well resolved and  $J_{\text{AB}} = 15.6$  Hz.

The unusual fact that in the 1-adamantyl cation **3a** the  $\gamma$  protons absorb at a lower field than the  $\beta$  ones has been explained in terms of a cage effect.<sup>9</sup> Originally, this effect was interpreted<sup>4</sup> in terms of an interaction of the "empty" p orbital of the trivalent carbocation center with the back lobes of three  $\text{sp}^3$  bridgehead C-H orbitals which converge toward the (tetrahedral) center of the molecule. This geometrically favored overlap would account



for selective sharing of the positive charge by the bridge-head positions. Indeed extended Hückel calculations suggest stabilization to the extent of 1.2 kcal/mole for such interactions.<sup>10,11</sup>

However, subsequent MO calculations by Hoffmann, Gleiter, and Heilbronner<sup>12-14</sup> indicated that such interactions are unlikely in adamantyl systems wherein the overlapping orbitals are intervened by only two bonds. More recent work by Sunko and Hehre<sup>15</sup> has pointed out that resonance structures such as  $\mathbf{3a} \leftrightarrow \mathbf{3a}'$  are responsible for the  $\gamma$ -deshielding effect. In a way this can



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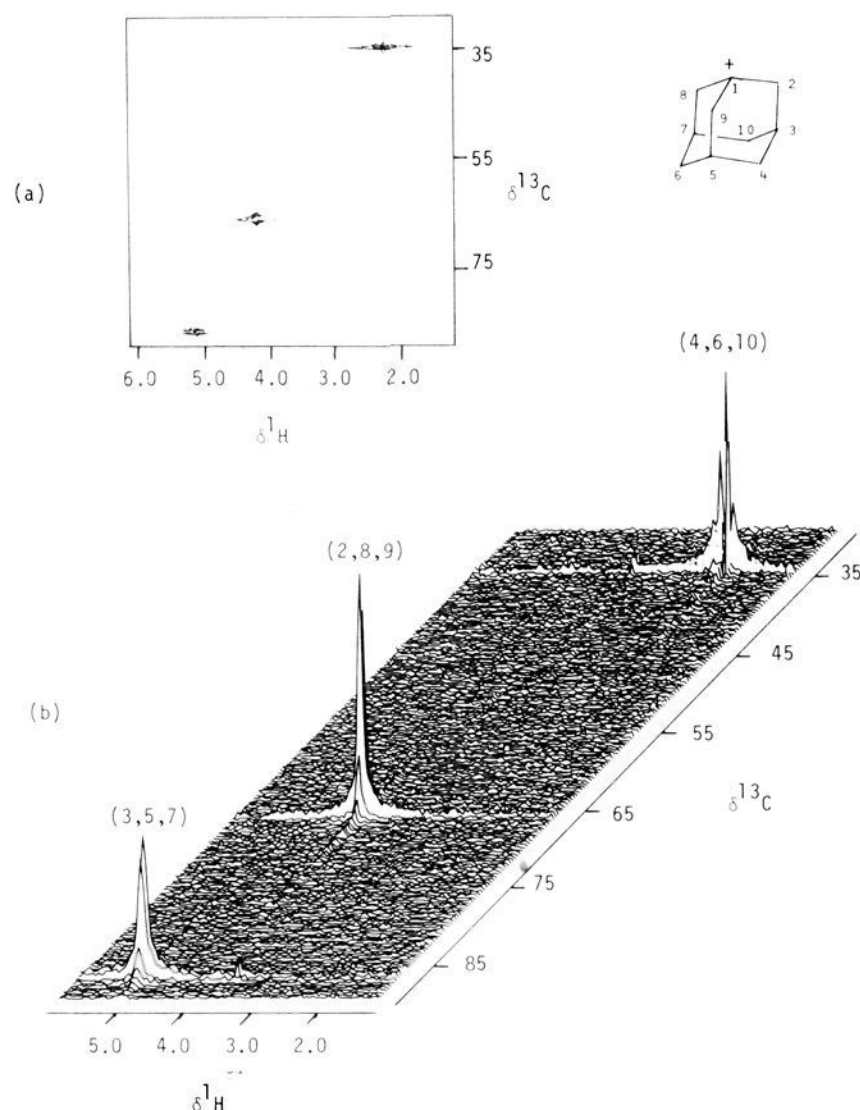
**Table I.** <sup>1</sup>H NMR Chemical<sup>a</sup> Shifts of Adamantyl, Diamantyl, Trimethylenenorbornyl, and Related Cations and Dications

cation or dication	temp, °C	H <sub>1</sub>	H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	H <sub>8</sub>	H <sub>9</sub>	H <sub>10</sub>	H <sub>11</sub>	H <sub>12</sub>	H <sub>13</sub>	H <sub>14</sub>	others
<b>3a</b>	-80		4.19	5.19	2.30	5.19	2.30	5.19	4.19	2.30	4.19					
<b>3b</b>	-80		3.79		1.85	5.00	2.13	5.00	4.09	2.13	4.09					CH <sub>3</sub> = 1.57
<b>3c</b>	-80		3.81		1.91		1.99	4.86	4.03	1.99	4.03					CH <sub>3</sub> = 1.71
<b>3d</b>	-80		3.77		1.93		1.93		3.77	1.93	3.77					CH <sub>3</sub> = 1.69
<b>12</b>	-60	4.18	2.80	2.80	4.18	br	br	1.65	3.40	2.36	3.40					
								1.50	2.80		2.80					
<b>6</b>	-80		3.79		4.16	5.04	2.05 ( <i>J</i> <sub>H-H</sub> = 12 Hz)	5.04	2.20 ( <i>J</i> <sub>H-H</sub> = 12 Hz)	2.20 ( <i>J</i> <sub>H-H</sub> = 12 Hz)	4.16					
<b>4</b>	-80		4.10	2.00	2.00	1.90	2.00	4.67	2.30	4.40	2.30	4.67	4.10	3.50	2.00	1.70 ( <i>J</i> <sub>AB</sub> = 18 Hz)
				1.70 ( <i>J</i> <sub>AB</sub> = 18 Hz)					2.10 ( <i>J</i> = 16 Hz)		2.10 ( <i>J</i> = 16 Hz)					

**Table II.** <sup>13</sup>C NMR Chemical Shifts<sup>a</sup> of Adamantyl, Diamantyl, and Trimethylenenorbornyl Cations and Related Dications

cation or dication	temp, °C	chemical shifts, ppm														others
		C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>14</sub>	
<b>3a</b>	-80	300	65.7	86.8	34.5	86.8	34.5	86.8	65.7	34.5	65.7					
			( <i>J</i> <sub>C-H</sub> = 147.6 Hz)			( <i>J</i> <sub>C-H</sub> = 149.8 Hz)				( <i>J</i> <sub>C-H</sub> = 129.5 Hz)						
<b>3b</b>	-80	298.7	73.2	99.2	42.8	84.6	35.8	84.6	66.7	42.8	66.7					CH <sub>3</sub> = 29.6
			( <i>J</i> <sub>C-H</sub> = 142.4 Hz)		( <i>J</i> <sub>C-H</sub> = 129.5 Hz)	( <i>J</i> <sub>C-H</sub> = 153.4 Hz)	( <i>J</i> <sub>C-H</sub> = 130.6 Hz)		( <i>J</i> <sub>C-H</sub> = 149.2 Hz)							( <i>J</i> <sub>C-H</sub> = 130.5 Hz)
<b>3c</b>	-80	296.2	71.8	94.0	49.1	94.0	41.8	79.9	65.4	41.8	71.8					CH <sub>3</sub> = 30.3
<b>3d</b>	-80	294.1	71.0	89.9	48.6	89.9	48.6	89.9	71.0	48.6	71.0					CH <sub>3</sub> = 30.1
																( <i>J</i> <sub>C-H</sub> = 128.6 Hz)
<b>12</b>	-29	59.7	32.6	32.6	59.7	194.0	194.0	31.4	46.1	28.7	46.1					
						( <i>J</i> <sub>C-H</sub> = 62 Hz)										
	-130 <sup>b</sup>	70.3		br		309.6	79.2		br							
<b>17</b>	-80	81.5	298.2	60.7	44.6	34.7	55.4	36.1	28.9	28.9	31.9					CH <sub>3</sub> = 31.9
<b>6</b>	-80	99.3	61.0	300.9	68.6	82.9	34.8	82.9	36.1	36.1	68.6					
<b>4</b>	-80	297.9	70.5	35.1	22.7	36.1	37.7	95.3	32.3	80.6	32.3	95.3	70.5	63.1	35.1	
<b>27</b>	-90	37.6	91.7	63.7	305.1	63.7	91.7	37.6	30.9	21.4	30.9	37.6	91.7	30.9	63.7	
<b>5</b>	-80	78.8	78.8	58.6	337.3	58.6	78.8	78.8	58.6	337.3	58.6	78.8	78.8	58.6	58.6	
<b>31</b>	-80	64.7	64.7	51.4	230.9	51.4	64.7	64.7	51.4	230.9	51.4	64.7	64.7	51.4	51.4	
<b>33-F</b>	-80 <sup>b</sup>	294.5		br	br	br	br	93.9	br	br	br	93.9	br	br	br	
<b>34-CH<sub>3</sub></b>	-80	53.7	73.5	312.4	59.3	47.5	34.5	53.7	33.9	22.0	32.7	34.2	34.5	33.9	47.5	CH <sub>3</sub> = 37.9
<b>34-C<sub>6</sub>H<sub>5</sub></b>	-80	49.7	59.3	265.1	46.1	45.7	34.5	49.7	35.6	22.8	33.7	34.5	34.5	35.6	45.7	ar, C <sub>p</sub> = 151.2, C <sub>o</sub> , C <sub>o'</sub> = 136.1, 135.9; C <sub>i</sub> = 134.9; C <sub>j</sub> = 130.7

<sup>a</sup>Chemical shifts are in ppm from external capillary tetramethylsilane. <sup>b</sup>Many peaks are too broad to assign.



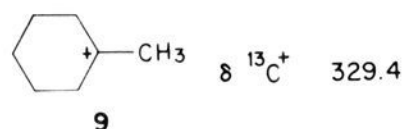
**Figure 3.**  $^1\text{H}$ - $^{13}\text{C}$  chemical shift correlated 2D NMR spectrum of 1-adamantyl cation in  $\text{SbF}_3/\text{SO}_2$  at  $-30^\circ\text{C}$ : (a) contour plot; (b) stacked plot.

be considered as a carbon-carbon hyperconjugation effect.

A similar  $\gamma$ -hydrogen deshielding effect is observed in 3-methyl-1-adamantyl cation **3b** and 3,5-dimethyl-1-adamantyl cation **3c** prepared from their bromo precursors ( $\delta$  5.00 for **3b** and 4.86 for **3c**), although in the latter two cations the charge is more delocalized on to the methyl-substituted bridgehead carbons.

These effects are more pronounced in the  $^{13}\text{C}$  NMR spectra of these cations. The 20-MHz  $^{13}\text{C}$  NMR spectrum of **3a** (Figure 2) in  $\text{SbF}_5/\text{SO}_2/\text{ClF}$  solution shows the following absorptions:  $\delta$   $^{13}\text{C}$  300 (s), 86.8 (d,  $J_{\text{C-H}} = 149.8$  Hz), 65.7 (t,  $J_{\text{C-H}} = 147.6$  Hz), and 34.5 (t,  $J_{\text{C-H}} = 129.5$  Hz). From the multiplicity data the chemical shifts can be readily assigned to  $\text{C}_\alpha$ ,  $\text{C}_\gamma$ ,  $\text{C}_\beta$ , and  $\text{C}_\delta$  carbons, respectively.

The assignment of the  $^{13}\text{C}$  resonances in **3a** were also correlated to their earlier assigned  $^1\text{H}$  resonances by obtaining its heteronuclear correlated 2D NMR spectrum<sup>16</sup> (Figure 3), recorded in  $\text{SbF}_5/\text{SO}_2$  at  $-40^\circ\text{C}$ . Figure 3 clearly indicates that the carbon resonating at  $\delta$   $^{13}\text{C}$  86.8 (d) is attached to a proton resonating at  $\delta$   $^1\text{H}$  5.19 (3 H). Similarly the carbon resonance at  $\delta$   $^{13}\text{C}$  65.7 (t) can be correlated to the proton resonance at  $\delta$   $^1\text{H}$  4.19 (6 H) and the carbon resonance at  $\delta$   $^{13}\text{C}$  34.5 (t) to the  $^1\text{H}$  AB quartet resonating at  $\delta$   $^1\text{H}$  2.30 (6 H). These correlations observed in the 2D NMR spectrum further prove the  $^{13}\text{C}$  and  $^1\text{H}$  NMR chemical shift assignments in **3a**. The observation of a greater deshielding of the more distant  $\text{C}_\gamma$  carbons than the  $\text{C}_\beta$  carbons which are adjacent to the carbocationic center is noteworthy. Also the  $\text{C}_\alpha^+$  carbocationic shift of  $\delta$  300 is more shielded than that in the model 1-methyl-1-cyclohexyl cation **9**.<sup>17</sup> The  $^{13}\text{C}$  NMR

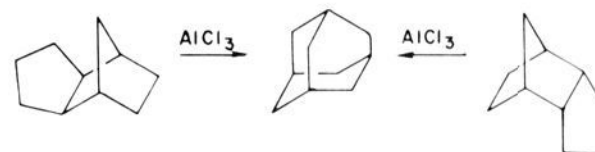


chemical shift shielding of  $\text{C}_\alpha^+$  and deshielding of  $\text{C}_\gamma$  is again best rationalized by the previously discussed carbon-carbon hyperconjugation effect.<sup>15</sup> It is interesting to note that  $\text{C}_\gamma$ 's are deshielded by 64.4 ppm, while  $\text{C}_\beta$ 's are deshielded by only 38.0 ppm in the 1-adamantyl cation **3a** compared to adamantane (**1**).

These effects are even more pronounced in the case of 3-methyl-, 3,5-dimethyl-, and 3,5,7-trimethyl-1-adamantyl cations (**3b**, **c**, and **d**, respectively). The  $\text{C}_\alpha^+$  carbocationic center is progressively shielded in their  $^{13}\text{C}$  NMR spectra. The chemical shifts range from  $\delta$  298.7 in **3b** to  $\delta$  294.1 in **3d** ( $\delta$  296.2 in **3c**). The gradual shielding of  $\text{C}_\alpha^+$  is due to the progressive methyl substitution at the bridgehead carbons. In fact, the bridgehead carbon ( $\text{C}_3$ ) bearing the methyl group in **3b** is observed at  $\delta$  99.2 due to the methyl substituent effect as well as  $\gamma$ -carbon deshielding effect due to C-C hyperconjugation.<sup>15</sup> In fact, in the neutral hydrocarbon series, one observes a deshielding of the  $\gamma$  carbons by only 1.4 ppm between adamantane and 1-methyladamantane.<sup>18</sup> Similarly, the chemical shifts of  $\text{C}_3$ ,  $\text{C}_5$  and  $\text{C}_3$ ,  $\text{C}_5$ ,  $\text{C}_7$  carbon atoms are also deshielded in **3c** and **d**, respectively ( $\delta$  94.0 and 89.9). The above observations again support the importance of mesomeric form **3a'** in stabilizing the bridgehead 1-adamantyl cation **3a** and related substituted adamantyl cations (**3b-d**).

We have also extended our studies to the isolation of the 1-adamantyl cation **3a** as its  $\text{SbF}_6^-$  salt and its solid-state  $^{13}\text{C}$  NMR spectrum. We obtained 50-MHz magic angle spinning cross-polarization  $^{13}\text{C}$  NMR spectrum of the bridgehead 1-adamantyl cation **3a** at room temperature. The  $\text{SbF}_6^-$  salt was prepared from 1-fluoroadamantane by using previously published procedure.<sup>19</sup> Except for some line broadening (line widths =  $\sim$ 50–80 Hz), the solid-state  $^{13}\text{C}$  NMR spectrum is almost identical with the solution spectrum in  $\text{SbF}_5/\text{SO}_2/\text{ClF}$  solution. The chemical shifts obtained in the solid state are  $\delta$   $^{13}\text{C}$  300, 89.7, 67.5, and 36.5. Apparently the dipolar interaction of the fluorines of the  $\text{SbF}_6^-$  counterion which results in a certain amount of line broadening did not cause much interference in the solid-state study. Other workers have circumvented this problem by broad-band fluorine decoupling,<sup>20</sup> adaptable, however, for only specialized instrumentation operating at low temperatures to dissipate excessive heat generated during decoupling.

**Study of the Formation of the 1-Adamantyl Cation 3a from Trimethylenenorbornane.** The acid-catalyzed isomerization of isomeric trimethylenenorbornanes to adamantane (**1**) not only opened up the chemistry of adamantanoid compounds but also represents one of the most fascinating intramolecular rearrangements known in carbocation chemistry.<sup>2a-c</sup> The mechanism of the rearrangement process has been studied in significant detail;<sup>21</sup> however, the possible direct observation of intermediate



carbocations along the isomerization path remained a long-standing challenge.

In  $\text{SbF}_5/\text{SO}_2$  solution at  $-78^\circ\text{C}$ , 2-*exo*-chloro-5,6-*exo*-trimethylenenorbornane (or 2-Br, 2-OH) first gave an intermediate cation **10**, which then rearranges to bridgehead 1-adamantyl cation **3a** around  $-30^\circ\text{C}$ . The solution of **10** kept below  $-50^\circ\text{C}$  in  $\text{SbF}_5/\text{SO}_2$  gave upon hydrolysis a single alcoholic product identified as 2,3-*endo*-trimethylene-2-*exo*-norbornanol (**11**).<sup>22a</sup> When

(18) Krishnamurthy, V. V.; Iyer, P. S.; Olah, G. A. *J. Org. Chem.* **1983**, *48*, 3373.

(19) Olah, G. A.; Svoboda, J. J.; Ku, A. T. *Synthesis* **1973**, 492.

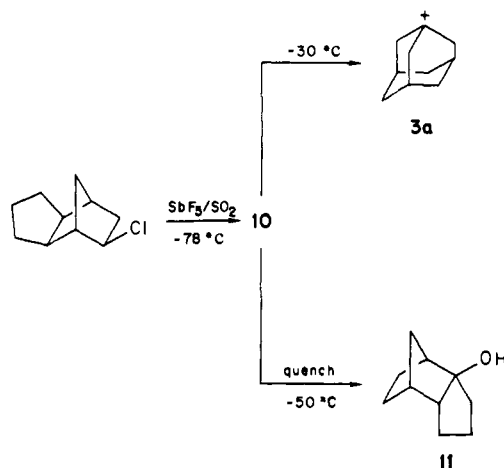
(20) Lyster, J. R.; Yannoni, C.; Fyfe, C. A. *Acc. Chem. Res.* **1982**, *15*, 208.

(21) (a) Schleyer, P. v. R.; Grubmüller, P.; Maier, W. F.; Vostrowski, O.; Skattebøl; Holm, K. H. *Tetrahedron Lett.* **1980**, 921. (b) Farcasiu, M.; Hageman, E. W.; Wenkert, E.; Schleyer, P. v. R. *Ibid.* **1981**, 1505. (c) Jäggi, F. G.; Ganter, C. *Helv. Chim. Acta* **1980**, *63*, 866. (d) Klester, A. M.; Jäggi, F. G.; Ganter, C. *Ibid.* **1980**, *36*, 1291. (e) Klester, A. M.; Ganter, C. *Ibid.* **1983**, *66*, 1200.

(22) (a) The structure is tentatively assigned as **11** (*endo*, *exo* stereochemistry) based on its  $^{13}\text{C}$  NMR spectrum. (b) Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5026.

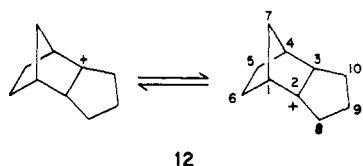
(16) (a) Maudsley, A. A.; Muller, L.; Ernst, R. R. *J. Magn. Reson.* **1977**, *28*, 463. (b) Bax, A. D.; Morris, G. A. *J. Magn. Reson.* **1981**, *42*, 501.

(17) Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1978**, *100*, 1487.



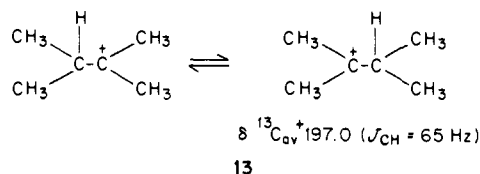
the ionization was carried out in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solution, the intermediate ion **10** was stable and did not rearrange to **3a** even at room temperature (25 °C) in a sealed NMR tube. The same ion **10** was obtained from various *exo*- or *endo*-trimethylene-norbornyl precursors.

The intermediate **10** generated in either  $\text{SbF}_5/\text{SO}_2$  or  $\text{SbF}_5/\text{SO}_2\text{ClF}$  showed identical  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. The 60-MHz  $^1\text{H}$  NMR spectrum of **10** at -60 °C in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solution consists of proton absorptions at  $\delta$  4.18 (2 H, br s), 3.40 (2 H, br), 2.80 (6 H, br), 2.36 (2 H, br s), 1.65 (1 H), and 1.50 (1 H, s). However, it was found that the  $^1\text{H}$  NMR spectrum was temperature-dependent. The quenching experiments does indicate that the structure of **10** probably is **12**. The 20-MHz  $^{13}\text{C}$  NMR



spectrum does support the structure **12**. At -29 °C, ion **10** in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  shows the following absorptions:  $\delta$   $^{13}\text{C}$  194.0 (d,  $J_{\text{C-H}} = 62$  Hz), 59.7 (d), 46.1 (t), 32.6 (t), 31.4 (t), and 28.7 (t). The observation of six peaks and the multiplicity data clearly support the equilibrating structure **12**. The observation of the most deshielded peak at  $\delta$   $^{13}\text{C}$  194.0 indicates a tertiary carbocationic center equilibrating with a secondary carbon atom, and the coupling of 62 Hz is an average of a secondary C-H coupling constant and a long-range tertiary C-C-H coupling. Similar chemical shifts have been observed, for example, in 2,3-dimethyl-2-butyl cation **13**.<sup>22b</sup>

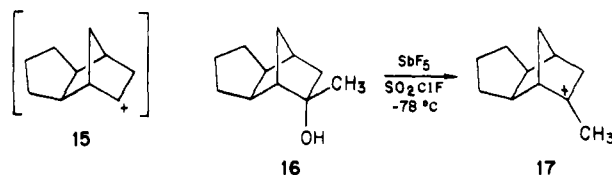
When the solution was cooled, the peaks at  $\delta$   $^{13}\text{C}$  194, 59.7, 46.1, and 32.6 broaden and merge into the base line, whereas the peaks at  $\delta$   $^{13}\text{C}$  31.4 and 28.7 remain relatively sharp. At -130



°C, the peak at  $\delta$   $^{13}\text{C}$  194 is split into two peaks at  $\delta$   $^{13}\text{C}$  309.6 and 79.2. The rest of the spectrum is too broad for proper assignments. This indicates that at this low temperature, the 1,2-hydride shift in **12** is frozen and a static (on the NMR time scale) 2,3-trimethylene-2-norbornyl cation **12** is obtained. From the temperature-dependent  $^{13}\text{C}$  NMR spectra between -29 and -130 °C, the coalescence temperature for the  $\text{C}_1$  and  $\text{C}_4$  carbons was found to be -110 °C. From the frequency separation between  $\text{C}_1$  and  $\text{C}_4$  carbons ( $\Delta\delta$ ) and coalescence temperature, an approximate energy barrier<sup>23a</sup> of  $\Delta G^\ddagger = 7.2 \pm 0.5$  kcal/mol for the 2,3-*exo*-hydride shift in **12** can be estimated. This value agrees very well with the barrier for the 2,3-*exo*-hydride shift in 2,3-

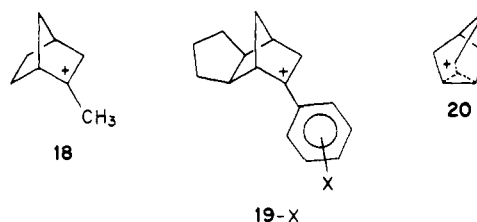
dimethyl-2-norbornyl cation **14** estimated by Sorensen<sup>23b</sup> ( $\Delta G^\ddagger = 7.2$  kcal/mol).

These observation indeed show that the structure of intermediate **10** is in fact **12**.<sup>23c</sup> To ascertain whether it is possible to obtain the 5,6-trimethylene-2-norbornyl cation **15**, we carried out ionization of 2-*exo*-chloro-5,6-*exo*-trimethylenenorbornane in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solution at -130 °C. However, even at this tem-



perature, only ion **12** was observed. On the other hand, ionization of 2-*exo*-methyl-5,6-*exo*-trimethylene-2-norbornanol (**16**) in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  at -78 °C gave 2-methyl-5,6-trimethylene-2-norbornyl cation **17**.

The 20-MHz  $^{13}\text{C}$  NMR spectrum of **17** showed nine absorptions at  $\delta$   $^{13}\text{C}$  298.2 (s), 81.5 (d), 60.7 (t), 55.4 (d), 44.6 (d), 36.1 (t), 34.7 (d), 31.9 (t, q), and 28.9 (t). The  $\text{C}_2$ ,  $\text{C}_1$ , and  $\text{C}_3$  carbons can readily be assigned to  $\delta$   $^{13}\text{C}$  298.2, 81.5, and 60.7, respectively. It is instructive to compare these chemical shifts with those of the analogous 2-methyl-2-norbornyl cation **18**,<sup>24a</sup> wherein the corresponding  $\text{C}_2$ ,  $\text{C}_1$  and  $\text{C}_3$  carbons are observed at  $\delta$   $^{13}\text{C}$  271.1, 80.3, and 55.6, respectively. The differences in chemical shifts



can be readily rationalized by the partial  $\sigma$ -bridged nature of **18**.<sup>24b</sup> A recent study of the application of Gassman-Fentiman tool of increasing electron demand by Farnum<sup>25</sup> on substituted 2-aryl-5,6-trimethylene-2-norbornyl cations **19-X** does indeed indicate less  $\sigma$ -bridging than in the corresponding 2-norbornyl cations. Consequently the parent ion **15** should also be less  $\sigma$ -bridged as the secondary 2-norbornyl cation **20**. However, the parent secondary cation **15** could not be prepared under stable ion conditions. The tertiary tricyclic cation **17** was found to be quite stable even at room temperature.

An unanswered question of the present study is why ion **12** rapidly rearranges to **3a** in  $\text{SO}_2$  solution and stays unrearranged in  $\text{SO}_2\text{ClF}$  solution. The difference in nucleophilicity and thus the solvating ability between  $\text{SO}_2$  and  $\text{SO}_2\text{ClF}$  may be responsible for this behavior.

**3,3'-(1,1'-Biadamantyl) Dication 6 and Attempted Preparation of 1,3-Adamantyl Dication 8.** The bridgehead dication **6** was obtained by dissolving 1,1'-biadamantane (**21**) in  $\text{SbF}_5/\text{SO}_2\text{ClF}$ . The dication **6** was also obtained by the ionization of 3,3'-dibromo-1,1'-biadamantane (**22**) under similar conditions. It is interesting to note that **6** did not undergo protolytic cleavage at the 1,1'-bond to yield **3a** even in  $\text{FSO}_3\text{H}/\text{SbF}_5$  solution. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of **6** are given in Tables I and II.

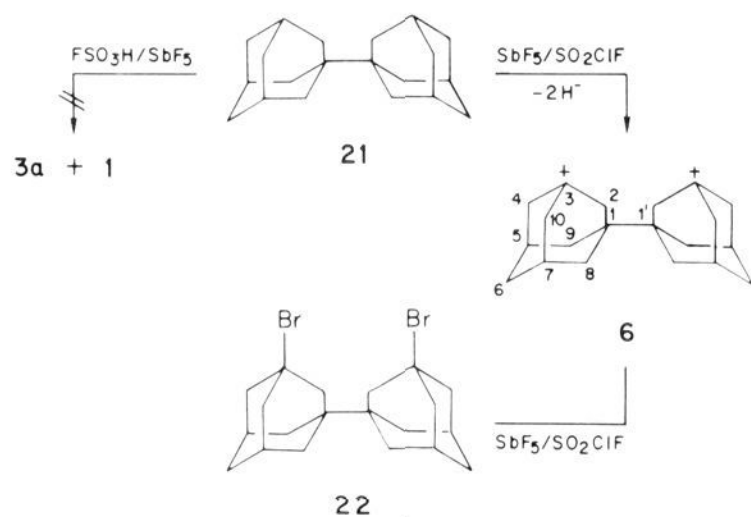
In the  $^{13}\text{C}$  NMR spectrum **6** shows seven absorptions characteristic of a monosubstituted bridgehead adamantyl cation. The two positive charges in **6** are significantly removed from each other (four carbons apart). The  $\text{C}_3$  cationic center at  $\delta$  300.9 is close to those observed for **3a** and **b**.

(23) (a) Sandstrom, J. "Dynamic NMR Spectroscopy"; Academic Press: New York, 1982. (b) Sorensen, T. S. *Acc. Chem. Res.* 1976, 9, 257. (c) Similar observations on **12** have been made by T. S. Sorensen (private communication).

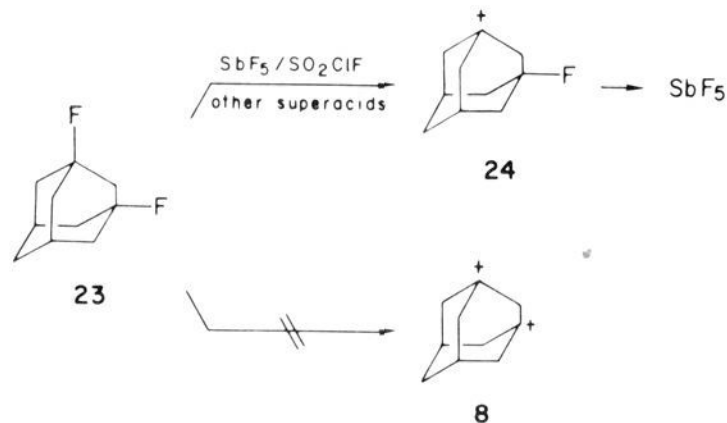
(24) (a) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Am. Chem. Soc.* 1977, 99, 5683. (b) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* 1980, 102, 683.

(25) Farnum, D. G.; Botto, R. E.; Chambers, W. T.; Lam, B. *J. Am. Chem. Soc.* 1978, 100, 3847.





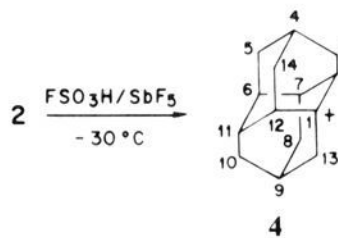
We also attempted to prepare the 1,3-adamantyl dication **8** from 1,3-difluoroadamantane (**23**) in a variety of superacid systems.



In all cases, however, only the monocation monodonor-acceptor complex **24** was obtained. These results indicate that the presence of two positive charges at the bridgehead positions separated by only one carbon atom would be too repulsive to allow formation of a stable dication. Earlier it has been demonstrated that alkyl-substituted trivalent dications can be generated only if the cationic centers are separated by at least two carbon atoms.<sup>26</sup>

**Bridgehead Diamantyl Cations.** Diamantane (**2**) can be viewed as the union of two adamantane units. Unlike adamantane (**1**), diamantane (**2**) (pentacyclo[7.3.1.1<sup>4,12</sup>.0<sup>2,7</sup>.0<sup>6,11</sup>]tetradecane), also called congressane,<sup>27</sup> after the emblem of the 1963 IUPAC congress which challenged its synthesis, contains two different types of tertiary hydrogen atoms (two apical bridgehead hydrogen atoms at the 4 and 9 positions and six belt hydrogen atoms at the 1,2,6,7,11, and 12 positions). It has been found that the belt position is more reactive than the apical centers in bromination reactions.<sup>28</sup>

In line with the above reaction, dissolution of diamantane (**2**) in neat  $\text{FSO}_3\text{H}/\text{SbF}_5$  results in the ionization of a belt hydrogen atom to give the 1-diamantyl cation **4**.<sup>5</sup> The structure of **4** was



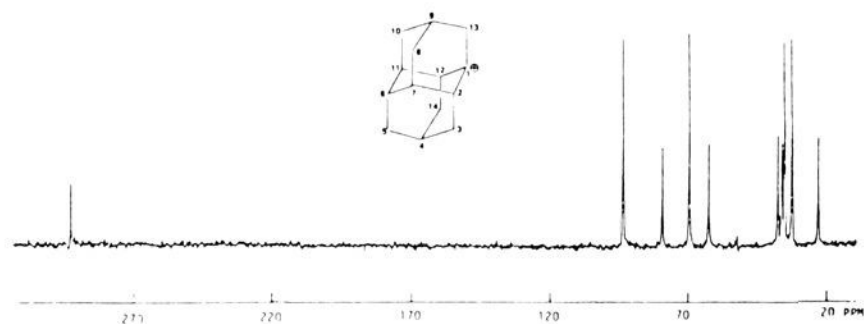
readily assigned based on the observed symmetry in the  $^1\text{H}$  NMR spectrum (Table I).

In analogy to the 1-adamantyl cation **3a**, the tertiary  $\text{H}_7$  and  $\text{H}_{11}$  atoms are assigned to the lowest field peak ( $\delta$  4.67) followed

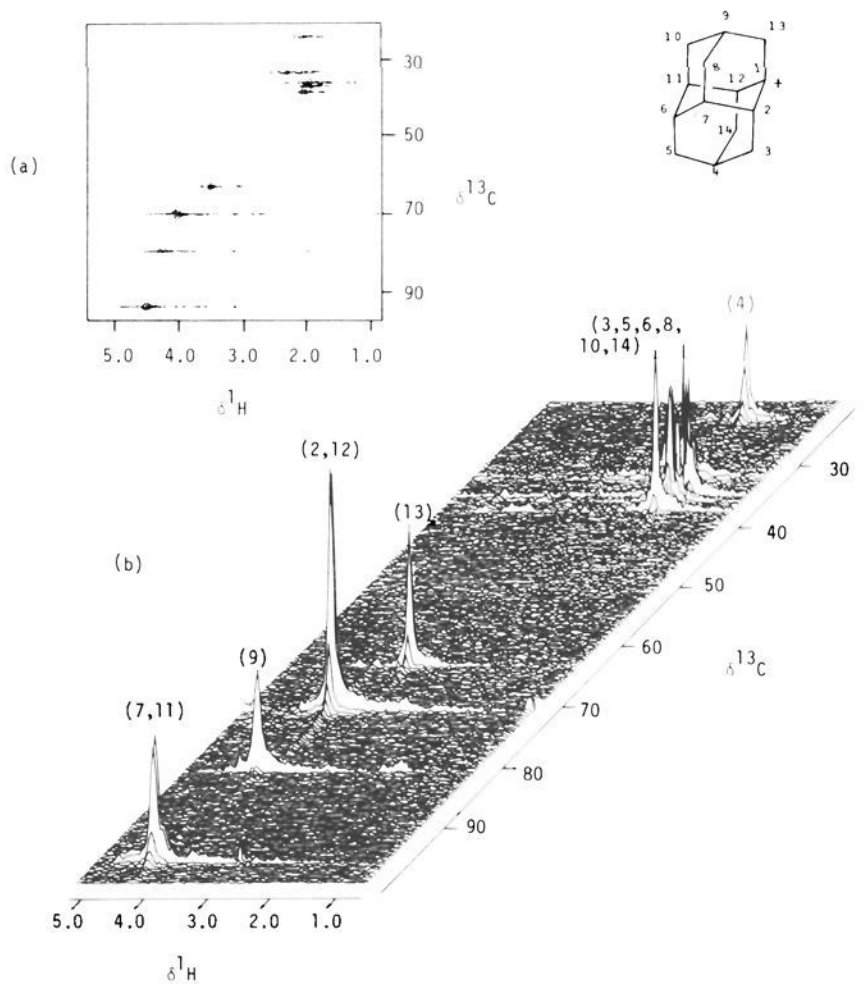
(26) Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 390.

(27) The structural formula of diamantane was chosen as the Emblem of the 19th IUPAC Congress in London in 1963 and called "congressane". The molecule was unknown at the time and the IUPAC committee had invited a synthesis as "a challenging objective for the participants in the congress". Diamantane was synthesized in 1965: Cupas, C.; Schleyer, P. v. R.; Trecker, D. J. *J. Am. Chem. Soc.* **1965**, *87*, 917.

(28) (a) Gund, T. M.; Schleyer, P. v. R. *Tetrahedron Lett.* **1973**, 959. (b) Gund, T. M.; Schleyer, P. v. R.; Unruh, G. D.; Gleicher, G. J. *J. Org. Chem.* **1974**, *39*, 2995.



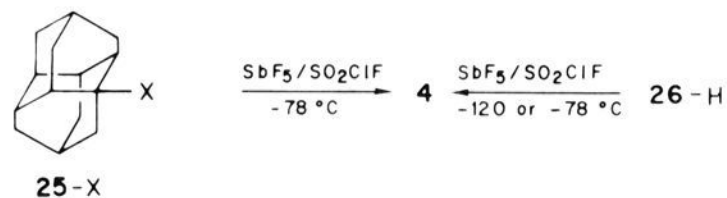
**Figure 4.** Proton-decoupled  $^{13}\text{C}$  NMR spectrum (20 MHz) of 1-diamantyl cation **4** in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  at  $-80^\circ\text{C}$ .



**Figure 5.**  $^1\text{H}$ - $^{13}\text{C}$  chemical shift correlated 2D NMR spectrum of 1-diamantyl cation in  $\text{SbF}_5/\text{SO}_2$  at  $-30^\circ\text{C}$ : (a) contour plot; (b) stacked plot.

by tertiary  $\text{H}_9$  atom at  $\delta$  4.40. Of the  $\alpha$ -hydrogen atoms  $\text{H}_2$  and  $\text{H}_{12}$  appear at  $\delta$  4.10 followed by  $\text{H}_{13}$  as a doublet at  $\delta$  3.50, coupled to  $\text{H}_9$ . All other hydrogen atoms ( $\text{H}_3$ ,  $\text{H}_4$ ,  $\text{H}_5$ ,  $\text{H}_6$ ,  $\text{H}_8$ ,  $\text{H}_{10}$ , and  $\text{H}_{14}$ ) appear as a multiplet centered at  $\delta$  2.03. These resonances have been resolved by using heteronuclear correlated 2D NMR, and all  $^1\text{H}$  resonances were assigned (vide infra).

The 1-diamantyl cation **4** can be obtained by the ionization 1-diamantyl derivatives **25-X** ( $\text{X} = \text{OH}$ ,  $\text{Br}$ , and  $\text{F}$ ) in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solution.<sup>8,9</sup> The same ion **4** was also obtained by the



$\text{X}: \text{OH}, \text{Br}, \text{F}, \text{Cl}$

ionization of 3-diamantanol **26-H** in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  analogous to the corresponding behavior of secondary 2-adamantyl derivatives<sup>8</sup> (vide infra).

The 20-MHz  $^{13}\text{C}$  NMR spectrum of **4** (Figure 4) in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  at  $-80^\circ\text{C}$  shows ten absorptions in agreement with its symmetry. Assignment of the individual carbons was made based on intensity and multiplicity data [and also based on its close resemblance to 1-adamantyl cation **3a**]. The chemical shifts are  $\delta^{13}\text{C}$  297.9 (s,  $\text{C}_1$ ), 95.3 (d,  $\text{C}_7$ ,  $\text{C}_{11}$ ), 80.6 (d,  $\text{C}_9$ ), 70.5 (d,  $\text{C}_2$ ,  $\text{C}_{12}$ ), 63.1 (t,  $\text{C}_{13}$ ), 37.7 (d,  $\text{C}_6$ ), 36.1 (t,  $\text{C}_5$ ), 35.1 (t,  $\text{C}_3$ ,  $\text{C}_{14}$ ), 32.3 (t,  $\text{C}_8$ ,  $\text{C}_{10}$ ), and 22.7 (d,  $\text{C}_4$ ).

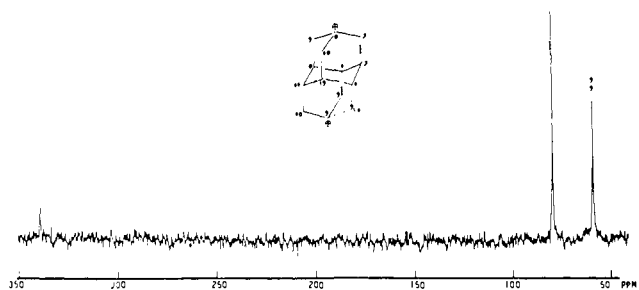
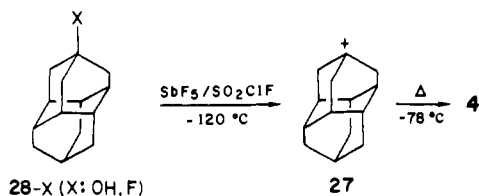


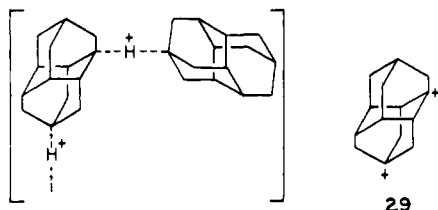
Figure 6. Proton-decoupled  $^{13}\text{C}$  NMR spectrum (20 MHz) of 4,9-diamantyl cation **5** in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  at  $-80^\circ\text{C}$ .

The 2D  $^{13}\text{C}$ - $^1\text{H}$  chemical shift correlation spectrum of 1-diamantyl cation in  $\text{SbF}_5/\text{SO}_2$  is shown in Figure 5. From the correlation peaks in 2D NMR and the  $^{13}\text{C}$  chemical shift assignment based on intensity and multiplicity data confirms our previous assignment of the  $^1\text{H}$  resonances, particularly the assignment of the lowest field peaks to the  $\gamma$ -hydrogen resonance. Moreover, one can also assign the  $^1\text{H}$  chemical shifts of all the proton within  $\pm 0.1$  ppm accuracy (cf. Table I). The two protons attached to  $\text{C}_3$  (as well as those to  $\text{C}_{14}$ ,  $\text{C}_8$ , and  $\text{C}_{10}$ ) are non-equivalent and as expected appear as a well-resolved AB quartet in the 2D spectrum, while they were unresolved multiplets centered at  $\delta$  2.03 in the  $^1\text{H}$  NMR spectrum.

Before discussing the  $^{13}\text{C}$  NMR chemical shift data, it is instructive to compare **4** with its apical bridgehead analogue, the 4-diamantyl cation **27**. The cation **27** was obtained by the

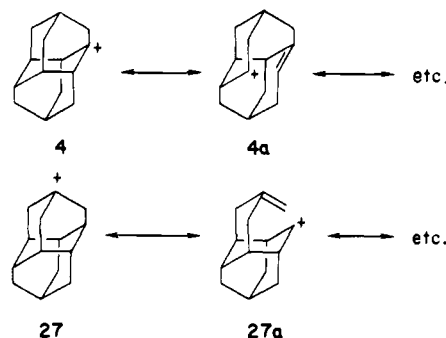


ionization of 4-diamantyl derivatives **28-X** in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  at  $-120^\circ\text{C}$ . Ion **27** is, however, rather unstable and smoothly rearranges to **4** at  $-78^\circ\text{C}$  (half-life  $\sim 3.5$  h). Consequently, it was impossible to obtain **27** devoid of traces of **4** even when the ionizations were carried out at  $-120^\circ\text{C}$ . This clearly indicates that the belt ion **4** is thermodynamically more stable than its apical isomer **27**. In fact, 4-diamantyl derivatives have been isomerized to 1-diamantyl derivatives by McKervery.<sup>29</sup> The rearrangement of **27** to **4** can be best rationalized by an intermolecular pathway rather than by intramolecular hydride shifts, similar to related rearrangements in the parent adamantane series. The facile intermolecular rearrangement of **27** to **4** even at  $-78^\circ\text{C}$  is surprising considering that the transition state for such a process is rather hindered and may involve a 1,4-dicationic intermediate **29**.<sup>28b</sup>

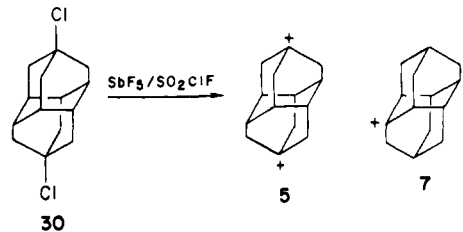


The  $^{13}\text{C}$  NMR spectrum of **27** at  $-90^\circ\text{C}$  shows six absorptions at  $\delta$   $^{13}\text{C}$  305.1 (s), 91.7 (d), 63.7 (t), 37.6 (d), 30.9 (t), and 29.4 (d). The apical carbocationic center and the  $\gamma$ -bridgehead carbons ( $\text{C}_2$ ,  $\text{C}_6$ , and  $\text{C}_{12}$ ) are more deshielded ( $\delta$   $^{13}\text{C}$  305.1 and 91.7) compared to those in the 1-adamantyl cation **3a**. In contrast, the belt carbocationic center in **4** is more shielded at  $\delta$  297.9. This is exactly the opposite trend observed in diamantane (**2**)<sup>31</sup> (the

apical carbon is more shielded than the belt carbon by 11.7 ppm). These differences can again be rationalized by a C-C hyperconjugative effect<sup>15</sup> in the cations. The mesomeric structure **4a** is more stabilized than **27a** due to substitution at the  $\alpha$  position in the former.



**4,9-Diamantyl Dication 5 and Attempted Preparation of 1,6-Diamantyl Dication 7.** As shown earlier, all our attempts to generate the 1,3-adamantyl dication **8** were unsuccessful. The "single-cage" hydrocarbon cannot accommodate two positive charges at the bridgehead position. However, diamantane provides a much larger separation in its expanded cage. It is, therefore, possible to accommodate a formal positive charge in each of the two fused adamantane cages. Clearly isomer **5** ("apical-apical")



should be the most stable since it would experience the least charge-charge repulsion. Apparently such charge repulsion would be maximum in the belt-belt isomer **7** and intermediate in apical-belt isomer **29**.

We have succeeded in preparing the 4,9-diamantyl dication **5** by the ionization of apical-apical 4,9-dichlorodiamantane (**30**) in  $\text{SbF}_5/\text{SO}_2\text{ClF}$ . The  $^{13}\text{C}$  NMR spectrum of **5** in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  at  $-80^\circ\text{C}$  (Figure 6) shows only three absorptions at  $\delta$   $^{13}\text{C}$  337.3 (s), 78.8 (d,  $J_{\text{C-H}} = 147.5$  Hz), and 58.3 (t,  $J_{\text{C-H}} = 147.5$  Hz). The high symmetry as well as the observation of highly deshielded carbocationic absorption clearly supports the formation of **5**. The bridgehead carbons (at  $\text{C}_1$ ,  $\text{C}_2$ ,  $\text{C}_7$ ,  $\text{C}_6$ ,  $\text{C}_{11}$ , and  $\text{C}_{12}$ ) are rather shielded as compared to those in either **3a** or **27**. This shows that due to the presence of two positive charges centered at  $\text{C}_4$  and  $\text{C}_9$  positions, the hyperconjugative stabilization by the  $\text{C}_\beta\text{-C}_\gamma$  bond may not be as important. This is again reflected by the large deshielding of the cationic center  $\delta$   $^{13}\text{C}$  337.3 compared to  $\delta$   $^{13}\text{C}$  300 in **3a** and  $\delta$   $^{13}\text{C}$  305.1 in **27**.

Surprisingly when the ionization of **30** is carried out in  $\text{SbF}_5/\text{SO}_2$  solution instead of  $\text{SO}_2\text{ClF}$ , a different  $^{13}\text{C}$  NMR spectrum was obtained. Although three peaks are still observed at  $\delta$   $^{13}\text{C}$  230.9 (s), 64.7 (d), and 51.4 (t) which are assigned to the  $\alpha$ ,  $\gamma$ , and  $\beta$  carbons, respectively,  $\text{C}_\alpha$  is highly shielded compared to that of **5** in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solution (by ca. 107 ppm). This indicates that the carbocationic center is significantly modified by complexation with more nucleophilic sulfur dioxide. This is the first example of the complexation of a tertiary carbocationic center by sulfur dioxide (although secondary and primary systems are known to interact). The observed dication in  $\text{SO}_2$  is assigned the structure **31**.

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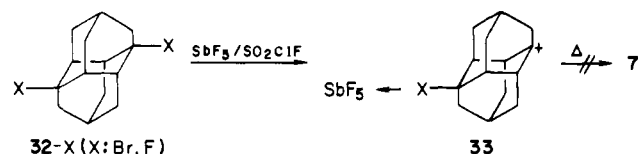
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The shielding of  $C_\alpha$  ( $C_4$  and  $C_9$ ) carbons is again reflected by the relative shielding of  $\beta$  and  $\gamma$  carbons. Charge-charge re-



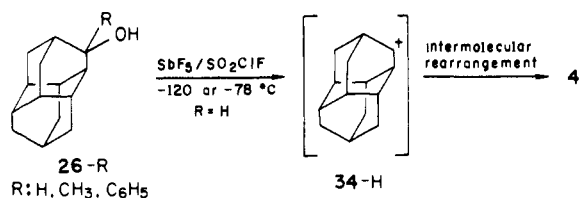
pulsion in dication **5**, as discussed, diminishes charge delocalization into the  $\sigma$  framework by C-C hyperconjugation, thus localizing the charge at the carbocationic centers and rendering them more reactive toward  $\text{SO}_2$ .

We also attempted to prepare the belt-belt isomeric 1,6-diamantyl dication **7** by the ionization of 1,6-dihalodiamantanes **32-X** ( $X = \text{Br}$  and  $\text{F}$ ) in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  and other superacids such



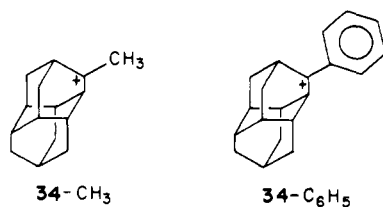
as  $\text{FSO}_3\text{H}$ :  $\text{SbF}_5/\text{SO}_2\text{ClF}$  and  $\text{HF}/\text{SbF}_5$  under various conditions. In all cases only the monocation monodonor-acceptor complex **33** was obtained, and the 1,6-dication **7** was not formed.

**3-Diamantyl Cations.** As mentioned before, dissolution of 3-diamantanol **26-H** in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  either at  $-78$  or  $-120$  °C gives only the rearranged bridgehead 1-diamantyl cation **4**. No



evidence was obtained for the intermediate secondary 3-diamantyl cation **34**. This rearrangement is similar to the rearrangement of the 2-adamantyl cation to **3a**.<sup>8,9</sup> The mechanism for such a rearrangement, considering the orientation of the orbitals involved, again probably occurs through an intermolecular rather than an intramolecular mechanism.<sup>8,9</sup>

On the other hand, dissolution of methyl-substituted **26-CH<sub>3</sub>** in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  at  $-78$  °C gave the 3-methyl-3-diamantyl cation **34-CH<sub>3</sub>**, which was found to be stable up to room temperature without undergoing any rearrangement or decomposition. The ion **34-CH<sub>3</sub>** shows the following <sup>13</sup>C NMR absorptions:  $\delta$  <sup>13</sup>C 312.4 (s), 73.5 (d), 59.3 (d), 53.7 (d), 47.5 (t), 37.9 (q), 34.5 (d), 34.2 (d), 33.9 (t), 32.7 (t), and 22.0 (d). The assignment of individual carbon atoms are shown in Table II. The cation **34-CH<sub>3</sub>** is comparable to 2-methyl-2-adamantyl cation,<sup>8</sup> although there



are some minor differences in the observed chemical shifts of the

former. The  $C_2$  and  $C_4$  carbon atoms which are  $\alpha$  to the cationic center in **34-CH<sub>3</sub>** are deshielded to a different degree ( $C_2$  at  $\delta$  73.5 and  $C_4$  at  $\delta$  59.3). This is in accordance with deshielding trend observed in the parent hydrocarbon diamantane **2** ( $C_2$  at  $\delta$  37.7 and  $C_4$  at  $\delta$  26.0).<sup>31</sup>

The 3-phenyl-3-diamantyl cation **34-C<sub>6</sub>H<sub>5</sub>** was also obtained by the ionization of **26-C<sub>6</sub>H<sub>5</sub>** in  $\text{SbF}_5/\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$  at  $-78$  °C. Ion **34-C<sub>6</sub>H<sub>5</sub>** is like any regular phenyl-substituted trivalent carbocation. The <sup>13</sup>C NMR spectrum of  $\text{C}_6\text{H}_5$ -**34** indicates extensive positive charge delocalization into the aryl ring (Table II). The para carbon is observed at  $\delta$  <sup>13</sup>C 151.2 which is close to that observed in 2-phenyl-2-adamantyl cation<sup>8</sup> ( $\delta$  154.2). Again one observes that the  $C_2$  and  $C_4$  carbons are deshielded differently (difference of 13.2 ppm) similar to that in neutral diamantane (**2**) (difference of 11.7 ppm).

### Conclusion

The bridgehead 1-adamantyl (**3a**), 3-methyl-1-adamantyl (**3b**), 3,5-dimethyl-1-adamantyl (**3c**), and 3,5,7-trimethyl-1-adamantyl (**3d**) cations were prepared in superacid medium and characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The bridgehead 1- and 4-diamantyl cations **4** and **27** were also prepared and characterized by NMR spectroscopy. The 4-diamantyl cation **27** slowly and irreversibly rearranges to the more stable 1-diamantyl cation, **4**. Ionization of the secondary 2-adamantyl and 3-diamantyl derivatives gives the corresponding bridgehead tertiary cations **3a** and **4**, respectively. The above rearrangements to the thermodynamically more stable bridgehead cations has been rationalized in terms of facile intermolecular hydrogen shifts.

The solid-state <sup>13</sup>C NMR spectrum of 1-adamantyl cation **3a** (as its  $\text{SbF}_6^-$  salt) was also recorded. Except for some line broadening, the solid-state <sup>13</sup>C NMR spectrum is almost identical with the solution spectrum in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solution. The 2D <sup>13</sup>C-<sup>1</sup>H chemical shift correlation spectra of 1-adamantyl and 1-diamantyl cations in  $\text{SbF}_5/\text{SO}_2$  were also obtained. The correlation peaks were used to assign many NMR chemical shifts. The relative deshielding of bridgehead  $\gamma$  carbons (and protons) with respect to  $\beta$ -methylenes in the bridgehead cations has been rationalized in terms of C-C hyperconjugation effect. 3,3'-(1,1'-Biadamantyl) dication **6** and 4,9-diamantyl dication **7** were also generated and studied. The charge-charge repulsion in **7** seems to diminish C-C hyperconjugative interaction which is found to be "operative" in all other bridgehead cations including **6**. Attempts to prepare 1,3-adamantyl and 1,6-diamantyl dications were, however, unsuccessful.

The equilibrating 2,3-trimethylene-2-norbornyl cation **12** is formed from the ionization of *exo*-5,6-trimethylene-2-norbornyl derivatives. The barrier for the degenerate 2,3-hydrogen shift has been estimated to be 7.2 kcal/mol. While cation **12** is quite stable in  $\text{SO}_2\text{ClF}$  solution even at room temperature, in  $\text{SO}_2$  it smoothly and irreversibly rearranges to 1-adamantyl cation **3a**.

### Experimental Section

The 1- and 2-adamantyl derivatives such as (chloro, bromo, and hydroxy compounds) were commercially available compounds. The 1- and 2-fluoroadamantanes were prepared by using  $\text{HF}/\text{pyridine}$  reagent<sup>32</sup> from their corresponding hydroxy derivatives. 1-Bromo-3-methyl-, 1-bromo-3,5-dimethyl-, and 1-bromo-3,5,7-trimethyladamantanes were prepared by the bromination<sup>33</sup> of the corresponding methyladamantanes (purchased from Aldrich Chemicals). The *exo*-chloro-, bromo-, and hydroxy-*exo*-trimethylenenorbornanes **9-X** were prepared according to the literature methods.<sup>34,35</sup> 2-Methyl-2-*endo*-hydroxy-5,6-*exo*-trimethylenenorbornane (**16**) (mp 78.5–79.5 °C) was prepared from 2-trimethylenenorbornanone<sup>35</sup> and methylmagnesium iodide in diethyl ether. 1,1'-Biadamantane (**21**) and 3,3'-dibromo-1,1'-biadamantane (**22**) were prepared from adamantane (**1**).<sup>36</sup> 1,3-Difluoroadamantane (**23**)<sup>27</sup>

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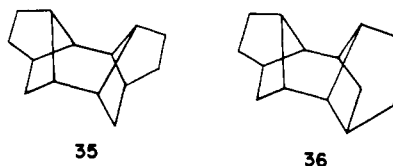
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was prepared from the readily available 1,3-dibromoadamantane.<sup>38</sup>

Diamantane (**2**) was prepared by the literature procedure<sup>39,40</sup> starting from the commercially available norbornadiene in three steps. The 1-diamantyl compounds **25-X** ( $X = \text{Cl}$  and  $\text{OH}$ ) and 4-diamantyl derivatives **28-X** ( $X = \text{Cl}$  and  $\text{OH}$ ) were prepared from diamantane.<sup>40</sup> The fluoro compounds **25-F** and **28-F** were synthesized from the corresponding bromo compounds<sup>28</sup> by using the modified Ritter-type reaction in  $\text{HF/pyridine}$  medium.<sup>41,42</sup> The 4,9-dichlorodiamantane (**30**) was obtained by the chlorination of tetrahydrobinor-S in  $\text{ClSO}_3\text{H}$ .<sup>43</sup> (One of the referees questioned the structure of tetrahydrobinor-S. Tetrahydrobinor-S is a  $\text{C}_{14}\text{H}_{20}$  hydrocarbon, whose exact structure<sup>45</sup> to date has not been determined. However, the two structures **35** and **36** have been proposed<sup>46</sup> based on the observation of seven  $^{13}\text{C}$  resonances.



To answer the question, we have carried out carbon-carbon connectivity studies by using C-C 2D<sup>47</sup> NMR experiment and found the structure to be **36** and not **35**.<sup>48</sup> 1,6-Difluorodiamantane **32-F** was synthesized from 1,6-dibromodiamantane **32-Br**.<sup>28</sup> 3-Diamantanone and 3-hydroxydiamantane **26-H** and **26-CH<sub>3</sub>** are known compounds.<sup>44,45</sup> The phenyl-substituted analogue **26-C<sub>6</sub>H<sub>5</sub>** was prepared by the addition of corresponding organo lithium compounds to 3-diamantanone in ether (**26-C<sub>6</sub>H<sub>5</sub>**, mp 111–112 °C). The new compounds **16** and **26-C<sub>6</sub>H<sub>5</sub>**, gave satisfactory spectroscopic and analytical data.

**Preparation of Carbocations and Carbodications.** Freshly distilled  $\text{SbF}_5$  and  $\text{FSO}_3\text{H}$  were used. To appropriate superacid dissolved in

twofold excess amount of  $\text{SO}_2\text{ClF}$  or  $\text{SO}_2$  at dry ice-acetone temperature ( $-78^\circ\text{C}$ ) or ethanol-liquid  $\text{N}_2$  slush ( $\sim -130^\circ\text{C}$ ) was slowly added with vigorous stirring a cooled slurry or solution of the appropriate precursor in  $\text{SO}_2\text{ClF}$  or  $\text{SO}_2$ , resulting in an approximately 10–15% solution of the cation or dication. The quenching experiment to obtain alcohol **11** was carried out by pouring the ion solution over crushed ice with rapid stirring. The aqueous layer was neutralized with solid  $\text{NaHCO}_3$  and extracted with ether which upon evaporation gave **11**.

$^1\text{H}$  NMR spectra were obtained either on a 60-MHz Varian A 56/60, 100-MHz Varian XL-100, or 200-MHz Varian XL-200 NMR spectrometers equipped with low-temperature probes. The 250-MHz spectra were recorded at Carnegie-Mellon University with an instrument equipped with a superconducting solenoid with a magnetic field of 58.7 kG.

$^{13}\text{C}$  NMR spectra were obtained on Varian Models, FT-80, XL-100, and XL-200 NMR spectrometers equipped with a low-temperature broad-band probe.

All the  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are referenced from external capillary tetramethylsilane.

**Heteronuclear correlated 2D NMR spectra** were recorded on a Varian XL-200 NMR spectrometer equipped with Nicolet Zeta-8 Model plotter at 50-MHz  $^{13}\text{C}$  resonance frequency. The pulse sequence used<sup>16</sup> is  $90^\circ(\text{H}) - (t_1)/2 - 180^\circ(\text{C}) - (t_1)/2 - \tau_1 - 90^\circ(\text{H}) 90^\circ(\text{C}) - \tau_2 - \text{FID}(t_2)$ , where  $t_1$  is the evolution period and  $t_2$  is the detection period during which broad-band  $^1\text{H}$  decoupling was performed. The experiment was performed in quadrature in both the proton and carbon dimensions, and the data were obtained by using a 4000-Hz spectral width for carbon and 1000-Hz spectral width for proton. For adamantyl cation **16**, transients were collected for each of 256 different values of the evolution period, and for the diamantyl cation **64** transients were collected for each of 128 different values of the evolution period. A Fourier number of 1K was used for transformation in both domain. Figures 3 and 5 show both the stacked plots and the contour plots. Chemical shifts were measured from the individual traces of the correlation peaks.

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**Registry No.** **2**, 2292-79-7; **3a**, 19740-18-2; **3a**· $\text{SbF}_6^-$ , 2062-52-4; **3b**, 72235-81-5; **3c**, 95531-29-6; **3d**, 95531-30-9; **4**, 95531-33-2; **5**, 95531-36-5; **6**, 95531-32-1; **7**, 95531-43-4; **8**, 95531-44-5; **9**, 26378-05-2; **11**, 86594-77-6; **12**, 95531-31-0; **16**, 27292-76-8; **17**, 95531-34-3; **21**, 3732-31-8; **22**, 15417-11-5; **23**, 54043-61-7; **Br-25**, 30545-17-6; **Cl-25**, 32401-16-4; **HO-25**, 30545-19-8; **F-25**, 77052-09-6; **CH<sub>3</sub>-26**, 30545-26-7; **C<sub>6</sub>H<sub>5</sub>-26**, 95531-42-3; **H-26**, 30545-24-5; **27**, 95531-35-4; **Br-28**, 30545-30-3; **Cl-28**, 32401-17-5; **F-28**, 77052-10-9; **HO-28**, 30651-03-7; **30**, 32401-20-0; **31**, 95531-37-6; **Br-32**, 32401-10-8; **F-32**, 90481-60-0; **F-33**, 95531-38-7; **H-34**, 95531-45-6; **CH<sub>3</sub>-34**, 95531-39-8; **C<sub>6</sub>H<sub>5</sub>-34**, 95531-40-1; **36**, 51966-18-8;  $\text{SbF}_5$ , 7783-70-2; norbornadiene, 121-46-0; 3-diamantanone, 30545-23-4; 2-*exo*-chloro-5,6-*exo*-trimethylenenorbornane, 56914-94-4; 1-fluoroadamantane, 768-92-3.

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