Preparation and ^{13}C NMR Spectroscopic Study of 2,6-Disubstituted 2,6-Adamantanediyl Dications[1]

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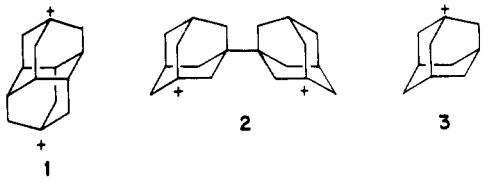
A series of 2,6-disubstituted 2,6-adamantanediyl dications 4-R has been prepared by the ionization of 2,6-disubstituted adamantane-2,6-diols 5-R in superacid media. The dications were stable only with stabilizing groups such as phenyl, cyclopropyl, and hydroxyl. The secondary dication 4-H and the tertiary 2,6-dimethyl-2,6-adamantanediyl dication 4-CH_3 could not be generated. The ^{13}C NMR spectroscopic study of the obtained dications clearly indicates that the positive charges are more delocalized into the substituents due to their close proximity in the adamantyl cage. Attempts to generate dipositive centers at the 1,4-position of the adamantyl skeleton were unsuccessful.

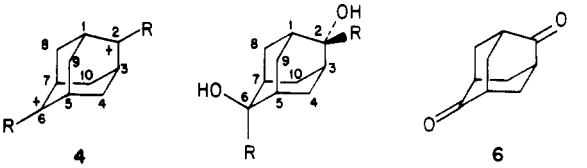
Studies on carbodications[2] are more limited as compared to those on carbomonocations. The first aliphatic carbodications were reported by Olah et al.[3] These studies showed that dipositive ions can be generated only if the carbocation centers are separated by at least two carbon atoms. An interesting example of bicyclic carbodications is the 1,5-bicyclo[3.3.3]undecanediyl dication[4] in which the bridgehead carbon atoms function as carbenium centers. Studies on 2,5-diaryl-2,5-norbornanediyl dications[5] and 2,6-disubstituted *anti*-bicyclo[5.1.0.0^{3,5}]octane-2,6-diyl dications[6] have also been reported.

Introduction of two cationic centers into the adamandoid skeleton has also been attempted and the diamantane-4,9-diyl cation, **1**, and 1,1′-biadamantane-3,3′-diyl dication, **2**, have been successfully prepared and studied by NMR spectroscopy. They show similar NMR spectral characteristics as the monopositive 1-adamantyl cation, **3**.[7]



1 **2** **3**

Our continued interest in the study of adamandoid hydrocarbons and their derivatives[7-10] prompted us to investigate the possibility of obtaining two cationic centers in a single adamantane skeleton. We now report the preparation and NMR spectroscopic investigation of 2,6-disubstituted 2,6-adamantanediyl dications, **4**.



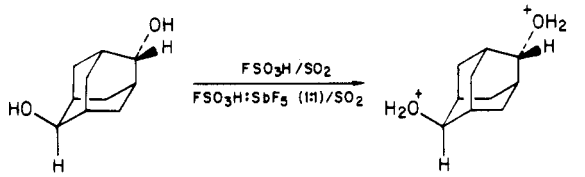
4 **5** **6**

R = H, CH_3, C_6H_5, *c*-C_3H_5, OH

Results and Discussion

The precursor alcohols, **5** (2,6-disubstituted adamantane-2,6-diols), were prepared by the reaction of adamantane-2,6-dione,[11] **6**, with the appropriate Grignard or alkyllithium reagents. The secondary diol, **5**-H, was obtained by $LiAlH_4$ reduction of the diketone. The ^{13}C NMR chemical shifts of these alcohols are listed in Table I. Characteristic of the C_2 symmetry, these diols show a 6-line pattern for the adamantane skeleton.

Attempted ionizations of the secondary diol, **5**-H, were unsuccessful. Both in FSO_3H/SO_2 and in SbF_5:FSO_3H (1:1)/SO_2 at −80 °C only the dioxonium ion **7** (i.e., diprotonated diol) could be observed. While the alcoholic



5-H **7**

carbons in the diprotonated species have the same chemical shifts (91.1 ppm) in both acid systems, other skeletal carbons show increased shielding in SbF_5:FSO_3H/SO_2 than in FSO_3H/SO_2 (cf. Table II). The chemical shift difference observed between the diol **5**-H and **7** in FSO_3H/SO_2 is comparable to that observed between 2-adamantanol and protonated 2-adamantanol in FSO_3H/SO_2 (cf. Table II), indicating similar behavior of the mono and the diol in this acid system. Increased shielding observed in the β and γ carbon atoms in the diprotonated diol, **7**, in SbF_5:FSO_3H/SO_2 is interesting and is probably due to the presence of bulky counterions tightly associated with the oxonium centers in magic acid compared to that in fluorosulfonic acid.

(1) Stable Carbocations, 263. For Part 262 see: Prakash, G. K. S.; Fung, A. P.; Rawdah, T. N.; Olah, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 2920.

(2) For a review, see: Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 390.

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Table I. ^{13}C NMR Chemical Shifts[a] of 2,6-Disubstituted 2,6-Adamantanediol 5-R and 2,6-Adamantanedione, 6

compd	$C_2(C_6)$	$C_1(C_7)$[b]	$C_3(C_5)$[b]	C_4	C_8	$C_9(C_{10})$	other
5-H	72.4	33.7	33.1	34.6	24.4	29.7	
5-CH_3	72.9	38.2	37.9	27.5	31.8	29.7	CH_3, 26.9
5-C_6H_5	74.7	34.7	34.5	27.8	31.8	29.8	C_2, 144.7; C_o, 125.4; C_m, 128.7, C_p, 127.4
5-c-C_3H_5	71.4	37.6	37.3	28.2	30.2	29.2	CH_2, 0.0; CH, 16.5
6	213.4	45.3	45.3	39.8	39.8	39.8	

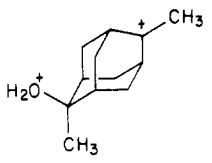
[a] All chemical shifts are in ppm (±0.1) in $CDCl_3$ at room temperature and are referenced to external Me_4Si; the assignments are based on the multiplicity in the APT[17] spectrum and the relative megnitude of the SCS values of the substituents.[8,18] [b] These chemical shifts can be interchanged.

Table II. ^{13}C NMR Chemical Shifts of the Dications 4-R, 7, and 8 and 2-Substituted 2-Adamantyl Cations 9-R

ion	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	other
4-C_6H_5	44.9	252.3	44.9	51.8	44.9	252.3	44.9	51.8	51.8	51.8	C_i, 137.2; C_o, 142.3; C_m, 133.8; C_p, 160.1
4-cC_3H_5	50.5	277.1	40.8	47.5	50.5	277.1	40.8	47.5	47.5	47.5	CH_2, 60.4; CH, 58.1
4-OH	42.5	247.7	42.5	44.3	42.5	247.7	42.5	44.3	44.3	44.3	
7[b]	29.8	91.1	29.2	33.3	29.2	91.1	29.8	23.7	28.5	28.5	
7	27.3	91.1	26.7	30.8	26.7	91.1	27.3	21.2	26.1	26.1	
8	58.0	321.0	57.3	42.2	32.4	100.1	32.4	39.5	39.5	42.2	C_2-CH_3, 40.4; C_6-CH_3, 20.2
9-CH_3[c]	66.3	323.0	66.3	52.6	29.1	36.6	29.1	52.6	52.6	52.6	CH_3, 41.2
9-C_6H_5[c]	51.4	271.3	51.4	49.3	29.5	36.3	29.5	49.3	49.3	49.3	C_i, 137.1; C_o, 138.1; C_m, 132.8; C_p, 154.2
9-cC_3H_5[d]	56.4	294.3	49.5	45.9	28.0	35.6	28.0	45.7	45.7	45.9	CH_2, 48.9; CH, 45.4
9-C_3H_5[e]	55.5	266.4	48.0	47.5	28.9	35.8	28.9	47.5	47.5	47.5	C_1, 139.0; C_2, 199.2; CH_3, 26.7
9-OH[c]	47.5	267.1	47.5	44.2	27.4	35.3	27.4	44.2	44.2	44.2	

[a] All chemical shifts are in ppm (±0.1) in 1:1 FSO_3H:SbF_5/SO_2 at −80 °C unless otherwise stated and are referenced to external Me_4Si. [b] In FSO_3H/SO_2. [c] Reference 12. [d] 2-Cyclopropyl-2-adamantyl cation in 1:1 FSO_3H:SbF_5/SO_2. [e] 2-(1-Propenyl)-2-adamantyl cation in 1:1 FSO_3H:SbF_5/SO_2ClF.

Attempted ionization of the dimethyl diol 5-CH_3 in SbF_5:FSO_3H (1:1)/SO_2 at −80 °C gave the monocation–monooxonium ion 8 as indicated by the presence of ^{13}C



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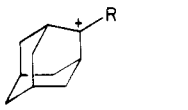

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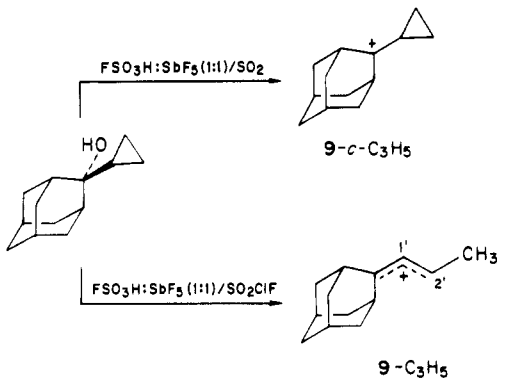
R = CH_3; C_6H_5; c-C_3H_5; OH

peaks at $\delta^{13}C$ 321 (C_2) and 100.1 (C_6). The cationic carbon (C_2) chemical shift is comparable to that observed in 2-methyl-2-adamantyl cation,[12] 9-CH_3 (cf. Table II). The alcoholic carbon (C_6) in 8 is deshielded by ~27 ppm when compared to that in 5-CH_3, clearly indicating that the hydroxyl group is protonated (or complexed) in this acid system. However, the deshielding observed on other carbon centers by the ionization of 5-CH_3 to 8 is much less when compared to that observed in the corresponding carbons by the ionization of 2-methyl-2-adamantanol[8] to 9-CH_3[12] (cf. Table II). For example C_1 is deshielded only by ~20 ppm on going from 5-CH_3 to 8 while it is deshielded by ~27 ppm on going from 2-methyl-2-adamantanol to 9-CH_3. However, the methyl group deshielding is comparable in both cases. The relatively less than expected deshielding observed in the skeletal carbons of 8 can again be due to the presence of the bulky counterions tightly associated with the oxonium center in magic acid. This behavior is complementary to that observed in diprotonated adamantane-2,6-diol, 7, in magic acid (vide supra).

Ionization of 2,6-diphenyladamantane-2,6-diol, 5-C_6H_5, in 1:1 SbF_5:FSO_3H/SO_2 cleanly gave the 2,6-diphenyl-2,6-adamantanediyl dication, 4-C_6H_5, as indicated by the presence of seven ^{13}C resonances (cf. Table II). The cationic carbons (C_2 and C_6) resonate at $\delta^{13}C$ 252.3, much shielded compared to the C_2 carbon ($\delta^{13}C$ 271.3)[12] in the monocation analogue, 2-phenyl-2-adamantyl cation, 9-C_6H_5. This indicates that the charge is delocalized more into the aryl ring in 4-C_6H_5 due to charge-charge repulsion. This increased charge delocalization is also reflected in the para carbon chemical shifts. Whereas the para carbon in 9-C_6H_5 resonates at $\delta^{13}C$ 154.2, it is more deshielded ($\delta^{13}C$ 160.1) in the dication, 4-C_6H_5.

We were also successful in generating the dicyclopropyl analogue, 4-c-C_3H_5, of 2,6-disubstituted 2,6-adamantanediyl dication, 4. In 1:1 FSO_3H:SbF_5/SO_2 the dicyclopropyl diol, 5-c-C_3H_5, ionizes cleanly to give the corresponding dication, 4-c-C_3H_5. In order to compare the ^{13}C chemical shift of the dication, 4-c-C_3H_5, we also prepared the corresponding monocation, namely, 2-cyclopropyl-2-adamantyl cation, 9-c-C_3H_5, from 2-cyclopropyl-2-adamantanol. The chemical shifts of both the mono- and the dication are listed in Table II. It must be pointed out that whereas in 1:1 FSO_3H:SbF_5/SO_2 the 2-cyclopropyl-2-adamantyl cation was formed cleanly from the 2-cyclopropyl-2-adamantanol, in SO_2ClF solvent only the rearranged 2-(1-propenyl)-2-adamantyl cation 9-C_3H_5 could be observed. It appears that in more nucleophilic SO_2 solvent[13] the more solvated cyclopropyl substituted cation 9-c-C_3H_5 survives while in less nucleophilic SO_2ClF



it rearranges to the more stable allylic cation, 9-C_3H_5. In the case of the dication, 4-c-C_3H_5, it could be generated

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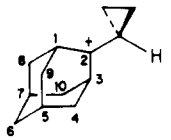
(13) Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 5163.

Table III. ^{13}C NMR Chemical Shifts[a] of Ions (Precursors) 11–15

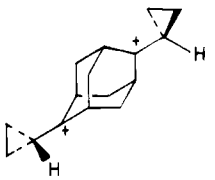
ion/compd	$C_1(C_3)$	C_2	$C_4(C_9)$	C_5	C_6	C_7	$C_8(C_{10})$	other
11[b]	65.4	314.3	63.1	92.6	37.6	32.7	38.3	CH_3, 40.0
12[b]	48.5	253.3	45.2	92.9	38.2	30.5	40.0	
	47.2							
13[c]	47.9	252.2	45.6	86.9	38.9	30.8	39.9	
14-Br[d]	48.9	214.3	48.8	59.9	47.7	31.2	37.4	
14-OH[d]	46.9	216.6	45.0	67.2	44.1	29.8	38.1	
15[d,e]	43.1	72.1	46.3	64.9	49.8	31.4	33.0	CH_3, 27.4, 26.8
	42.7	71.8	44.2	64.5	49.7	31.0	30.9	

[a] All chemical shifts are in ppm (±0.1) and are referenced to external Me_4Si. [b] In FSO_3H:SbF_5 (1:1)/SO_2 at −80 °C. [c] In FSO_3H/SO_2 at −80 °C. [d] In $CDCl_3$ at room temperature. [e] Two isomers.

only in SO_2 solvent and all attempts to generate it in SO_2ClF and observe the diallylic dication were unsuccessful. Both the monocation 9-c-C_3H_5 and the dication 4-c-C_3H_5 show nonequivalence of the bridgehead carbons (C_1 and C_3) because of hindered rotation due to cyclopropyl conjugation. In 9-c-C_3H_5 even the β-methylenes are nonequivalent (C_4, C_{10} and C_8, C_9) and appear as two ^{13}C resonances at $\delta^{13}C$ 45.9, 45.7. One would also expect nonequivalence of the methylene carbons in 4-c-C_3H_5 and there should be three carbon resonances for the methylene in the ^{13}C spectrum. However, they could not be resolved and appear as a slighly broad peak at $\delta^{13}C$ 47.5.



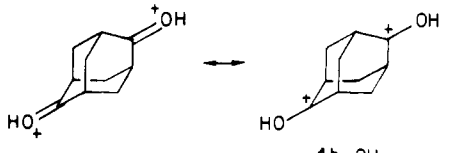
9-c-C_3H_5



4-c-C_3H_5

The cationic carbon in 9-c-C_3H_5 resonates at $\delta^{13}C$ 294.3, while in 4-c-C_3H_5 it is much shielded and appears at $\delta^{13}C$ 277.1, clearly indicating that in the dication, due to charge–charge repulsion, there is increased cyclopropyl conjugation. This is also reflected in the cyclopropyl carbon resonances at $\delta^{13}C$ 48.9 (t) and 45.4 (d) in 9-c-C_3H_5 and at 60.4 (t) and 58.1 (d) (more deshielded) in 4-c-C_3H_5.

Dissolution of the diketone **6** in 1:4 SbF_5:FSO_3H/SO_2 at −80 °C gave the corresponding 2,6-dihydroxy-2,6-adamantanediyl dication, **4**-OH. Again, a comparison of the ^{13}C chemical shift of the C_2 and C_6 carbons in **4**-OH to that in protonated adamantanone, **9**-OH, reveals that the positive charges in **4**-OH reside mostly on the oxygen atoms, with increased contribution from the carboxonium resonance structure, **4a**-OH. The carbonyl carbons are much more shielded ($\delta^{13}C$ 247.7) in **4**-OH compared to that in **9**-OH ($\delta^{13}C$ 267.1).[12]

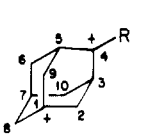


4a-OH **4b**-OH

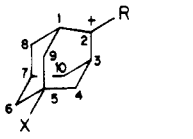
We were thus successful in generating two tertiary cationic centers at the C_2 and C_6 positions of the adamantane skeleton. However, the dications were stable only with a strongly stabilizing group such as phenyl, cyclopropyl, or hydroxyl. Previous attempts to prepare the bridgehead 1,3-adamantyl dication have been unsuccessful.[14] This 1,3-dication, separated only by a methylene group, obviously could not overcome excessive charge–charge repulsion.

(14) Mateescu, G. D. Ph.D. Dissertation, Case Western Reserve University, 1971.

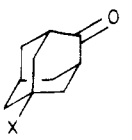
We also attempted to prepare 1,4-dications, i.e., the 4-substituted 1,4-adamantanediyl cations, **10**. 5-Bromo-



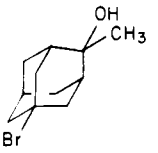
10
R = CH_3; OH



11, R = CH_3; X = Br → SbF_5
12, R = OH; X = Br → SbF_5
13, R = OH; X = $^+OH_2$



14
X = Br; OH



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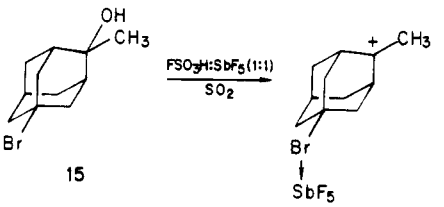
2-methyl-2-adamantanol, **15**, the precursor for 4-methyl-1,4-adamantanediyl dication, **10**-CH_3, was prepared by the reaction of methyllithium with 5-bromoadamantanone,[14] **14**-Br, at low temperature. Attempts to ionize **15** in 1:1 FSO_3H:SbF_5 in SO_2 gave only the monocation-monocomplex, **11**, as indicated by the ^{13}C resonances at $\delta^{13}C$ 314.3,



15 **11**

92.6, 65.4, 63.1, 40.0, 38.3, 37.6, and 32.7 (cf. Table III). The cationic carbon resonance at $\delta^{13}C$ 314.3 is characteristic of the 2-methyl-2-adamantyl cation and the resonance at $\delta^{13}C$ 92.6 is attributed to the bridgehead carbon containing the bromine atom which is complexed to acid. All attempts to force the ionization of the bridgehead bromine by warming up the SO_2 solution were, however, unsuccessful. In order to stabilize the positive charge at the 4-position and thus increase the chances of ionization, we attempted to ionize the bromo ketone, **14**-Br, and the hydroxy ketone, **14**-OH, in 1:1 FSO_3H:SbF_5/SO_2. However, these attempts gave either **12** or **13** and no **10**-OH could be observed. The ^{13}C chemical shifts of the precursors (**14** and **15**) and those of **11**, **12**, and **13** are listed in Table III. Thus we were unable to generate dicationic species at 1,4-position in adamantyl skeleton even by stabilizing one of the cationic center as a carboxonium moiety.

Conclusions

In conclusion we successfully prepared and characterized by ^{13}C NMR spectroscopy 2,6-disubstituted 2,6-

adamantanediyl dications, the first examples of dipositive ions with two cationic centers in a single adamantane skeleton. Such dications are, however, stable only when the 2,6-tertiary cationic centers are substituted by stabilizing groups such as phenyl, cyclopropyl, and hydroxyl. ^{13}C NMR spectroscopic study of the obtained dications indicates that the positive charges are significantly delocalized into the substituents due to their close proximity in the adamantyl cage. Attempts to generate related dications at the 1,4-position of the adamantyl skeleton were unsuccessful.

Experimental Section

Adamantane-2,6-dione, **6**, was prepared by literature procedure[11] starting from Meerwein's ester. Reaction of the diketone with excess methyllithium, phenyllithium, or cyclopropyl-Grignard reagent in THF gave the corresponding dimethyl, diphenyl, and dicyclopropyl diols **5**. $LiAlH_4$ reduction of the diketone in THF gave the secondary diol, **5**-H. 5-Bromoadamantanone was prepared by direct bromination of adamantanone according to literature procedure.[15] Reaction of the bromo ketone with methyllithium at 0 °C in ether gave 5-bromo-2-methyl-2-adamantanol. 5-Hydroxyadamantanone was obtained by nitric acid oxidation of 2-adamantanone.[16] All the new compounds (i.e., **5**-c-C_3H_5, **5**-C_6H_5, and **15**) gave satisfactory elemental analysis and their ^{13}C NMR chemical shifts are listed in Tables I and III along with the data for other compounds.

Preparation of Carbocations and Carbodications. Freshly distilled SbF_5 and FSO_3H were used. To appropriate superacid dissolved in twofold excess amount of SO_2ClF or SO_2 at −80 °C was slowly added with vigorous stirring a cooled slurry or solution of the appropriate precursor in SO_2ClF or SO_2 resulting in an approximately 10–15% solution of the cation or dication.

^{13}C NMR spectra were obtained on Varian Models FT-80 and XL-200 NMR spectrometers equipped with low-temperature broad band probes. The ^{13}C NMR chemical shifts are referenced from external capillary tetramethylsilane.

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Furans in Synthesis. 5.[1] Furan-Terminated Cationic Cyclizations in the Preparation of Fused, Spirocyclic and Bridged Ring Systems. An Application to the Synthesis of Nakafuran 9

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The title compounds **36–42** and nakafuran 9 (**43**) were prepared by furan-terminated cationic cyclizations. The cyclization substrates, allylic alcohols **16**, **17**, **25**, **26**, **33**, and **34**, and the derived enone **19** were prepared by CuCN moderated S_N2' addition of Grignard reagents derived from 2-(3-furyl)-1-bromoethane (**12**) and 3-(3-furyl)-1-bromopropane (**13**) to vinyl epoxides **14** and **22** and epoxy enol ether **21**. Treatment of substrate allylic alcohols with a two-phase mixture of HCO_2H and cyclohexane resulted in facile cyclization when the forming ring was six or seven membered. Enone closures proceeded only when a six-membered ring was produced or in the case of enone **48** which leads to nakafuran 9 (**43**).

The exploitation of cationic π-cyclizations in the construction of polycyclic ring systems has been the object of intense study since the early 1950s.[3] While the methodology for the preparation of fused-ring systems has been well developed and extensively utilized relatively few general srategies for the construction of spiro[4] and bridged systems[5] have been developed. Therefore, there remains a need for methodology which facilitates the preparation

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