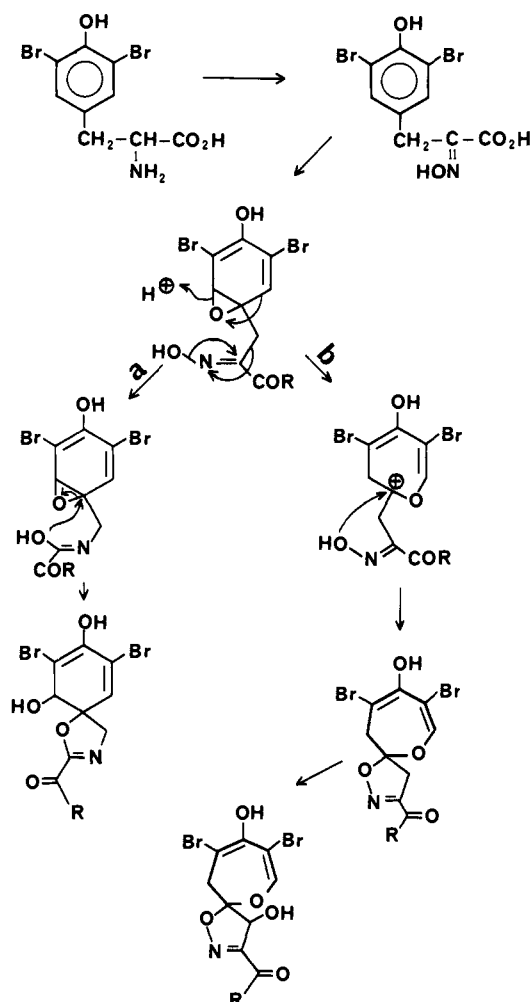**Scheme I**

196 (9), 194 (100), 192 (17); 179 (9), 177 (18), 175 (8); 169 (4), 167 (19), 155 (45); 127 (38), 125 (43); 113 (9), 111 (12).

CIMS *m/z* 441, 439, 437 (2 Br), 407, 405, 403 (2 Br), 340, 338, 336 (2 Br), 249, 247 (1 Br), 233, 231 (1 Br), 221, 219 (1 Br).

HRFDMS *m/z* 749.8308 (M^+ + H, $C_{21}H_{24}{}^{79}Br_2{}^{81}Br_2N_3O_7$, calcd 749.830 68).

Psammaplysin-B Acetamide Diacetate (8b). T.. 12.9 mg of **8a** in 0.5 mL pyridine cooled in acetone/dry ice Ac_2O (0.5 mL) was added, and the reaction mixture was warmed to room temperature. The solution was stirred for 1 h, when **8a** was completely converted to a less polar compound (based on TLC; silica, R_f = 0.19, CH_2Cl_2/EtOAc, 1:1). Toluene was added, and the resulting azeotrope was evaporated in vacuo. The crude product was purified on a silica gel column (CH_2Cl_2/EtOAc, 1:1) to give **10b** as a colorless oil; amorphous solid from acetone/H_2O, mp 84–87 °C; $[\alpha]^{22}{}_D$ −44.5° (*c* 1.93, MeOH).

IR ($CHCl_3$) 3400, 2950, 1760, 1680, 1550, 1460, 1380, 1200, 1100, 1000, 930 cm^{-1}.

UV (CH_3CN) λ_{max} 225 sh (ε 8000), 228 sh (12 500), 229 (18 700), 231 sh (17 500), 238 sh (12 300), 243 sh (9400), 253 sh (7400), 268 sh (5700), 276 sh (4100), 282 sh (2700).

^{1}H NMR ($CDCl_3$) δ 7.46 (2 H, s), 7.13 (1 H, t, *J* = 5.8), 7.02 (1 H, s), 6.37 (1 H, s), 5.81 (1 H, t, *J* = 5.8), 5.67 (1 H, dd, *J* = 4.2, 8.2), 4.05 (2 H, t, *J* = 5.7), 3.68 (2 H, dd, *J* = 5.8, 6.7), 3.63 (3 H, s), 3.59 (1 H, dd, *J* = 4.2, 5.8), 3.48 (1 H, dd, *J* = 5.8, 8.2), 3.17, 3.02 (2 H, AB q, *J* = 16.0), 2.19 (3 H, s), 2.10 3 H, s), 2.06 (2 H, overlapping t, *J* = 5.7, 6.7), 1.95 (3 H, s).

EIMS *m/z* 421 (8%), 419 (11), 417 (6) 2 Br cluster; 379 (6), 377 (9), 375 (6) 2 3r cluster; 366 (2), 364 (3), 362 (1) 2 Br cluster; 296 (2), 294 (4), 293 (7), 292 (1), 291 (4) overlapping 2 and 1 Br clusters; 273 (2), 271 (3), 269 (2) 2 Br cluster; 258 (5), 256 (8), 1 Br cluster; 214 (4), 212 (3); 194 (6), 192 (6).

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anti-Tricyclo[5.1.0.0³,⁵]octa-2,6-diyl Dications. Novel Bis(cyclopropylcarbinyl) Dications[1a]

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Abstract: A series of 2,6-*anti*-tricyclo[5.1.0.0³,⁵]octa-2,6-diyl dications **4-R** have been prepared by the ionization of related diols **5-R** in superacid solutions and characterized by ^{13}C and ^{1}H NMR spectroscopy. All attempts to generate the parent secondary dication **4-H** and observe its potential degenerate circumambulatory rearrangement (cyclopropylcarbinyl type) were, however, unsuccessful. Only ring-opened homotropylium cation **8** was observed. However, a series of tertiary dications were successfully prepared and studied by ^{13}C and ^{1}H NMR spectroscopy, showing significant positive charge delocalization into the annulated cyclopropane rings.

The structure and facile interconversion of cyclopropylcarbinyl and cyclobutyl cations have been well documented.[2,3] Previously we reported[4] the dynamic behavior of 2-bicyclo[4.1.0]heptyl cations **1** under stable ion conditions. The 2-bicyclo[4.1.0]heptyl

1, R=H,CH₃ **2**

3

4, R= H,CH₃,C₆H₅,cC₃H₅ and OH
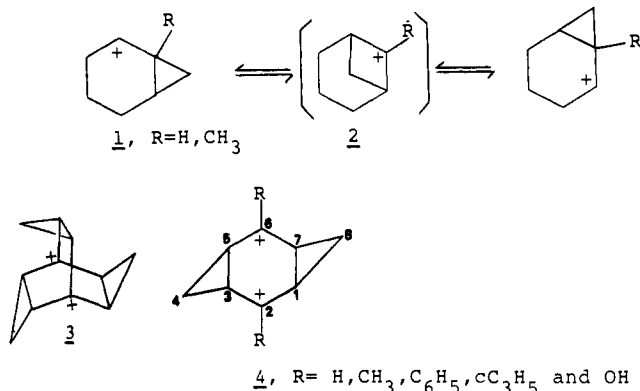
cation 1-H underwent a degenerate equilibration involving an unpopulated (high-lying) bicyclo[3.1.1]heptyl cation (cyclobutyl cation) **2**. However, it was possible to freeze out this equilibration [$\Delta G^\ddagger$(−85 °C) = 8.50 ± 0.5 kcal/mol] at lower temperatures. Prompted by the above study, we now wish to report preparation and ^{13}C and ^{1}H NMR spectroscopic characterization of 2,6-*anti*-tricyclo[5.1.0.0³,⁵]octadiyl dications **3**, a class of novel bis-(cyclopropylcarbinyl) dications. In contrast to the present study, the attempts to generate the related 1,5-trishomobarrelene dication **3** has remained futile.[5a] In general, compared to studies on carbocations, the investigation of carbodications is more limited. The field has been recently reviewed.[5b]

Results and Discussion

The starting precursor diols **5-R** were prepared[6] from the corresponding Grignard reactions with *anti*-tricyclo[5.1.0.0³,⁵]-octa-2,6-dione (**6**).[7] The secondary alcohol **5-H** was synthesized by the sodium borohydride reduction of **6**.[6] The secondary

**5**, R=H,CH₃,C₆H₅,cC₃H₅ **6** **7**
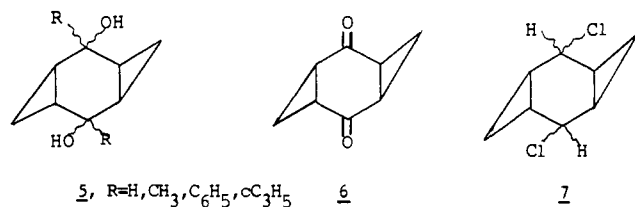
dichloro compound **7** was obtained by treating **5-H** with dry HCl in benzene.[6] In all cases, the precursors **5-R** and **7** were obtained as a mixture of cis and trans isomers,[6] and they were used as such in the ionization studies without separation.

The ionizations were carried out in superacidic SbF₅/SO₂ClF or SbF₅:FSO₃H(1:1)/SO₂ClF solutions at either −78 or −120 to −130 °C and ^{13}C NMR spectra recorded over the temperature range of −120 to 0 °C. The ^{13}C NMR data of the observed

carbocations and dications are given in Table I along with their chemical shift assignments. The assignments were made by comparison with model carbomonocations and based on multiplicities observed in off-resonance decoupled spectra. ^{1}H NMR spectra were recorded at −85 °C and the data are presented in the individual discussion sections.

The ionization of the parent secondary diol **5-H** in SbF₅/SO₂ClF or SbF₅:FSO₃H/SO₂ClF even at −120 °C yielded as the only product the known homotropylium ion **8**.[8] The same ion
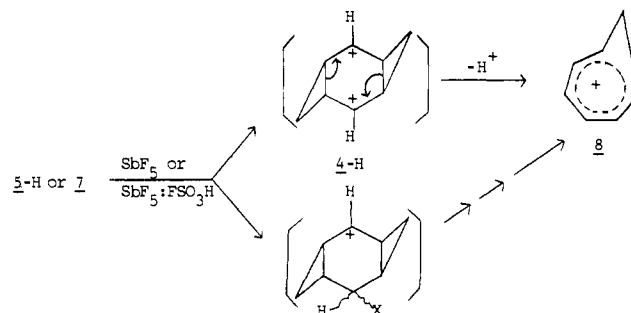
8 was also obtained when the ionization of the parent dichloride precursor **7** was carried out in SbF₅/SO₂ClF at −120 °C. The formation of the tropylium ion **8** can be rationalized via the dicyclopropyldicarbinyl cation **4-H**, which upon ring expansion and deprotonation would yield homotropylium cation **8**. Alternatively, **8** can be formed involving stepwise ionization, ring expansion, and deprotonation. All attempts to observe **4-H** by further lowering the temperature of ionization (−130 °C) as well as changing the solvent to a mixture of SO₂ClF:SO₂F₂ were unsuccessful.

The elusive dicyclopropyldicarbinyl dication **4-H** is interesting not only because it is a dipositive ion but also because it is capable of undergoing circumambulatory rearrangement of the type shown below. This process seems possible in view of the facile degenerate

4-H
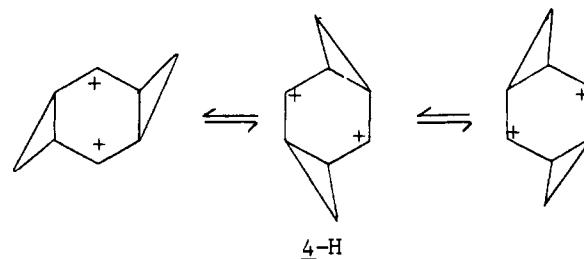
cyclopropylcarbinyl rearrangement observed in the case of the monocation analogue, the 2-bicyclo[4.1.0]heptyl cation **1-H**.[4]

As the parent secondary system gave no observable dication, we attempted ionization of related tertiary systems. The ionization of **5-CH₃** in SbF₅/SO₂ClF at −120 °C gave indeed the 2,6-di-methyl-*anti*-tricyclo[5.1.0.0³,⁵]octa-2,6-diyl dication **4-CH₃**. The proton decoupled ^{13}C NMR spectrum showed four absorptions at δ ^{13}C 293.4 (s), 55.9 (t), 48.4 (q), and 43.0 (d). The large deshielding of C₄ and C₈ cyclopropane methylenes is indicative of significant positive charge delocalization into the cyclopropane rings. In the ^{1}H NMR spectrum, **4-CH₃** showed, following absorptions at δ ^{1}H 4.08 (br, 4 H), 3.48 (br, $J_{H-H} \geq 9$ Hz, 2 H), 3.10 (s, 6 H), and 2.71 (br, $J_{H-H} \geq 6$ Hz, 2 H). The peak at δ ^{1}H 4.08 is readily assigned to ring methine protons. The endo (inside) and exo (outside) methylene protons of the annulated cyclopropane rings are assigned δ ^{1}H 3.48 and 2.71, respectively. These ^{1}H NMR assignments are based on the assignments of *anti*-tricyclo-[5.1.0.0³,⁵]octa-2,6-dione protons by Dreiding and co-workers[7] based on the magnitude of coupling constants. The methyl protons at δ 3.48 are characteristic of a methyl group adjacent to a carbocationic center. It is instructive to compare the ^{13}C chemical

(1) (a) Considered Stable Carbocations. 262. For part 261, see: Prakash, G. K. S.; Arvanaghi, M.; Olah, G. A. *J. Am. Chem. Soc.*, in press. (b) University of Southern California. (c) Present address: Department of Chemistry, University of Petroleum and Minerals, Dhahran, Saudi Arabia.

(2) For major reviews, see: Haywood-Farmer, J. *Chem. Rev.* **1974**, *74*, 315. Wilberg, K. B.; Hess, B. A., Jr.; Ashe, A. J. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 26. Hanack, M.; Schneider, H. J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 666. Breslow, R. In "Molecular Rearrangements"; de Mayo, I. P., Ed.; Wiley-Interscience: New York, 1963; Part I, Chapter 4.

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(5) (a) de Meijere, A. *Angew. Chem.* **1979**, *91*, 867. (b) Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 390.

(6) Kessler, H.; Ott, W. *Tetrahedron Lett.* **1974**, 1383.

(7) Heller, J.; Yoger, A.; Dreiding, A. S. *Helv. Chim. Acta* **1972**, *55*, 1003.

(8) (a) Winstein, S. *Q. Rev. Chem. Soc.* **1969**, *23*, 141. (b) Olah, G. A.; Staral, J. S.; Liang, G. *J. Am. Chem. Soc.* **1974**, *96*, 6233. (c) Olah, G. A.; Liang, G.; Paquette, L. A.; Broadhurst, M. J.; Warner, P. *Ibid.* **1973**, *95*, 3386.

Table I. ^{13}C NMR Chemical Shifts[a] of Observed Carbocations and Carbodications in SbF_5/SO_2ClF or $SbF_5:FSO_3H/SO_2ClF$

| ion	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	others
4-CH₃	43.0	293.4	43.0	55.9	43.0	293.4	43.0	55.9	CH₃ = 48.4
11	182.0	135.9	148.6	135.9	182.0	89.0	42.0	89.0	CH₃ = 27.6
4-C₆H₅	35.8	235.4	35.3	46.3	35.3	235.4	35.3	46.3	C₆H₅: C_p = 155.5; C_m = 133.9; C_o = 140.8; C_i = 130.1
4-cC₃H₅	29.6[b]	260.8	27.3[b]	37.9[d]	27.3[c]	260.8	29.6[c]	35.5[d]	cC₃H₅: α-CH = 54.9; β-CH₂ = 53.8, 52.5
4-OH	28.3	226.5	28.3	28.3	28.3	226.5	28.3	28.3	

[a] Chemical shifts in parts per million from external capillary tetramethylsilane.   [b-d] Assignments interchangeable.

shifts of **4-CH₃** with those of monocation analogue 2-methyl-2-bicyclo[4.1.0]heptyl cation **9**.[4] It appears that positive charge
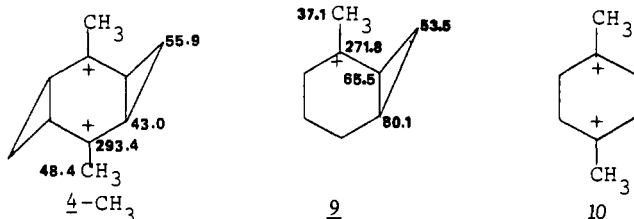
in the monocation is much more dispersed into the annulated cyclopropane ring than that in the presently studied dication **4-CH₃** as shown by the ^{13}C chemical shifts of the cationic centers (δ^{13}C 271.8 for **9** and 293.4 for **4-CH₃**). This is also reflected by the corresponding methyl carbon chemical shifts (δ^{13}C 37.1 in **9** and 48.4 in **4-CH₃**). This is easily rationalized by the presence of two positive charges separated only by two carbon atoms, which leads to a substantial degree of charge–charge repulsion. Hence delocalization into the cyclopropane rings puts significant positive charge at C_1, C_3, C_5, and C_7 positions, respectively, which can lead to destabilization. However, it appears that dication **4-CH₃** derives significant stability by partially delocalizing its positive charge into cyclopropane rings. In fact, previous attempts to generate unstabilized 2,4-dimethylcyclohexyl-2,6-diyl dication **10** under stable ion conditions were unsuccessful.[9a]

The dication **4-CH₃** upon warming to −30 °C for several hours (≈4 h) irreversibly rearranges to 1,5-dimethylhomotropylium cation **11**. The formation of **11** from **4-CH₃** can be rationalized
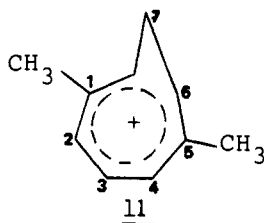

by ring expansion and deprotonation mechanism. The cation **11** is highly symmetrical in nature, showing six ^{13}C NMR absorptions at δ^{13}C 182.0 (s), 148.6 (d), 135.1 (d), 89.0 (d), 42.0 (t), and 27.6 (q). The formation of **11** is further supported by its characteristic ^{1}H NMR spectrum at −85 °C. The 1,5-dimethylhomotropylium cation, **11**, had the following ^{1}H NMR shifts: δ[1]H 6.97 (s, 3 H), 4.14 (t, J_{H-H} = 9.4 Hz, 2 H), 3.89 (br, 1 H), 1.88 (s, 6 H), and −1.23 (br, 1 H). The protons at δ[1]H 6.97 and 4.14 are readily assigned to the H₂, H₃, H₄ and H₆, H₈ sets of protons, respectively. The endo and exo methyl protons at C₇ are observed at δ[1]H −1.23 and 3.89, indicating a definite ring current effect for the endo proton of the homotropylium skeleton.[8]

Dissolution of phenyl-substituted diol **5-C₆H₅** in SbF₅:FSO₃H/SO₂ClF at −78 °C yielded the 2,6-diphenyl-*anti*-tricyclo[5.1.0.0³,⁵]octa-2,6-diyl dication **4-C₆H₅**. The dication showed seven absorptions in its ^{13}C NMR spectrum; δ^{13}C 235.4 (s), 155.5 (d), 144.8 (d), 133.9 (d), 130.1 (s), 46.3 (t), and 35.3 (d). The observation of the para carbon at δ 155.5 and the cyclopropane methylene at δ 46.3 is indicative of positive charge dispersal into both phenyl as well as cyclopropane rings, although
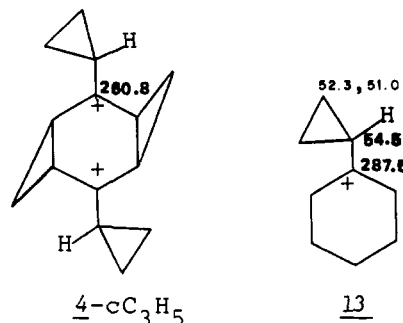
(9) (a) Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N. *J. Am. Chem. Soc.* **1980**, *102*, 6127. (b) The 1,4-cyclohexanedione has the following ^{13}C NMR absorptions in CDCl₃ at 24 °C: δ^{13}C 208.3 (s) and 36.3 (t).

more charge is delocalized into the former than latter. This effect is also reflected by the ^{1}H NMR spectrum of **4-C₆H₅**: δ[1]H 8.1 (d, J_{H-H} = 7.9 Hz, 2 H, ortho), 7.89 (t, J_{H-H} = 6.7 Hz, 1 H, para), 7.34 (t, 2 H, meta), 4.0 (d of d, $J_{H-H_{exo}}$ = 6.5, $J_{H-H_{endo}}$ = 9.5 Hz, 4 H, ring protons), 3.02 [(d of t, $J_{H-H_{exo}}$ = 5, $J_{H-H_{endo}}$ = 9.5 Hz, 2 H, H_{endo} (inside)], and 2.32 [(d of t, $J_{H-H_{endo}}$ = 5, $J_{H-H_{ring}}$ = 6.5 Hz, 2 H, H_{exo} (outside)].

Comparing **4-C₆H₅** to its previously studied analogue 1,4-diphenyl-1,4-cyclohexyl dication **12**,[9a] one finds that more positive charge delocalized into the phenyl ring of the latter as reflected by the para carbon chemical shifts (δ^{13}C 160.1). However, in
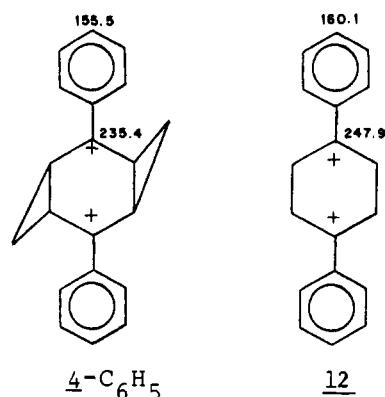
the former dication **4-C₆H₅**, the cationic center is much more shielded (by 12.5 ppm) compared to those in **12**, indicating additional stabilization by the cyclopropane rings. The dipositive ion **4-C₆H₅** was found to be extremely stable and did not decompose or rearrange even when warmed to 0 °C.

The 2,6-dicyclopropyl-*anti*-tricyclo[5.1.0.0³,⁵]oct-2,6-diyl dication, **4-cC₃H₅**, was obtained by the ionization of the corresponding 2,6-dicyclopropyl diol **5-cC₃H₅** in SbF₅/SO₂ClF at −78 °C. The dipositive ion **4-cC₃H₅** showed eight ^{13}C NMR absorptions (Table I), indicating that cyclopropyl substituent at the 2 and 6 positions introduces asymmetry on the tricyclic ring carbons. The observation of the cationic center at δ^{13}C 260.8, and the α-CH and β-CH₂ of substituent cyclopropyl group at δ^{13}C 54.9 (d), 53.8 (t), and 52.5 (t), indicate substantial charge delocalization into the free cyclopropyl groups. Additionally, the positive charge is also dispersed into the annulated cyclopropane rings [δ^{13}C 37.9, 35.5 (t) and 29.6, 27.3 (d)]. A comparison of the ^{13}C NMR chemical shifts of dication **4-cC₃H₅** with those of 1-cyclopropyl-1-cyclohexyl cation **13**[4] indicates some interesting differences. In the latter monopositive cation, the cationic center

was observed at δ^{13}C 287.5, although the cyclopropyl group carbon chemical shifts were similar to those in **4-cC₃H₅**. Almost 26.7

ppm shielding of the cationic center observed in **4-cC₃H₅** compared to that in **13** has to be due to charge dispersal into the annulated cyclopropane rings. The ¹H NMR spectrum of **4-cC₃H₅** was rather complex and was difficult to make unequivocal assignments. The following absorptions were observed for **4-cC₃H₅**: δ¹H 3.22 (br m, 4 H), 2.94 (s, 8 H), 2.64 (br d, 2 H), 2.35 (d, 2 H), and 1.47 (m, 2 H).

Protonation of the *anti*-tricyclo[5.1.0.0³,⁵]octa-2,6-dione **6** in FSO₃H/SO₂ClF at –78 °C gave the diprotonated species **4-OH**. At –80 °C, the ¹³C NMR spectrum of **4-OH** showed only two absorptions at δ¹³C 226.5 (s), 28.3 (t, d), indicating that proton on the oxygen is still exchanging. Lack of significant deshielding of cyclopropane carbons seems to indicate that dipositive ion **4-OH** exists predominantly as a dicarboxonium ion species **4-OH(A)** and not as dihydroxycarbenium ion species **4-OH(B)**. The ob-

4-OH (A)   4-OH (B)

4-OH (C)   4-OH (D)
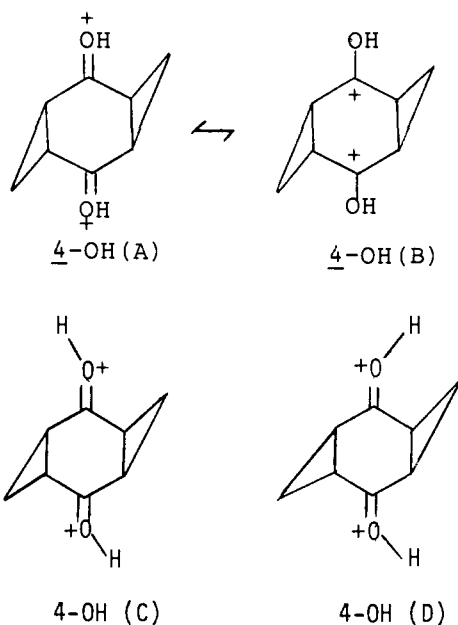
served deshielding of carbonyl carbon in **6**[10] upon protonation to

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(10) The dione **6** showed the following ¹³C NMR absorptions in CDCl₃ solution at 27 °C: δ¹³C 201.3 (s), 24.6 (d), and 13.2 (t).

4-OH of 25.2 ppm is somewhat smaller than that observed in the case of cyclohexanedione (34 ppm).[9] In the ¹H NMR spectrum, the proton on oxygen in **4-OH** was observed only in FSO₃H: SbF₅/SO₂ClF solutions. In fact two signals at δ¹H 13.47 and 13.44 (in the ratio 1:1) were observed for **4-OH** in FSO₃H: SbF₅/SO₂ClF, indicating the existence of two structural isomers **4-OH(C)** and **4-OH(D)** in the medium. This is further supported by the observation of two set ring methine protons at δ¹H 2.73 and 2.61. However, the methylene exo (outside) and endo (inside) protons do not show any separate signals for the individual isomers. These were observed at δ¹H 1.78 and 2.23, respectively.

The presently studied novel 2,6-*anti*-tricyclo[5.1.0.0³,⁵]octa-2,6-diyl dications represent a fascinating new class of bis(cyclopropylcarbinyl) dications. Whereas the parent secondary ion **4-H** rearranges exceedingly readily to the homotropylium ion **8** and could not be observed even at –130 °C, tertiary ions **4-CH₃**, **4-C₆H₅**, and **4-cC₃H₅** could be prepared and studied under stable conditions.

Experimental Section

Precursor diols **5-H**, **5-CH₃**, and **5-C₆H₅** and dichloride **7** were prepared from the *anti*-tricyclo[5.1.0.0³,⁵]octa-2,6-dione **6**[7] following a literature procedure.[6] All these compounds were obtained as mixture of cis and trans isomers and were used as such. The dicyclopropyl-substituted diol **5-cC₃H₅** was obtained by the addition of cyclopropylmagnesium bromide to **6** in tetrahydrofuran. The diol **5-cC₃H₅** was again obtained as a mixture of cis and trans isomers and showed characteristic spectroscopic properties; mp 121–122 °C (uncorrected); ¹H NMR δ (CDCl₃) 1.03 (br s, 2 H, OH), 1.0 (m, 4 H, ring protons), 0.4–0.7 (complex m, 14 H, other cyclopropane protons); IR (KBr) 3570 (OH), 2990–3030 (cyclopropane CH), 1030 cm⁻¹ (cyclopropane CH).

Preparation of Ions. The appropriate precursor dissolved in SO₂ClF, precooled at –78 °C (in a dry ice–acetone bath), is slowly added with vigorous stirring to a freshly prepared solution of a fourfold excess of SbF₅/SO₂ClF, SbF₅:FSO₃H/SO₂ClF, or FSO₃H/SO₂ClF maintained at either –78 °C or –120 to –130 °C (in a liq. N₂/ethanol slush bath) in a 10-mm NMR tube so as to obtain approximately 10–15% solution of the ion.

¹³C and ¹H NMR spectra were recorded on a Varian Associates Model FT-80 spectrometer and XL-200 spectrometer, respectively, equipped with a variable temperature broad-band probe. The chemical shifts are in parts per million from external capillary tetramethylsilane.