^{13}C NMR Spectroscopic Study of Potential Tris- and Bishomocyclopropenyl Cations[2]

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Abstract: The effect of methyl and phenyl substituents, in comparison with the parent systems, was determined by ^{13}C NMR spectroscopic study of potentially homoaromatic carbocations, obtained upon ionization of the corresponding bicyclo[3.1.0]hexyl and 4-cyclopentenyl alcohols and chlorides, respectively. Winstein's parent trishomocyclopropenyl cation **3**, first obtained as a stable ion by Masamune via ionization of *cis*-bicyclo[3.1.0]hex-3-yl chloride **4**-Cl was also independently prepared from *cis*-bicyclo[3.1.0]hexan-3-ol **4**-OH in protic acid free SbF_5/SO_2ClF solution at −78 °C. Ion **3**, once formed, was found stable upon addition of Brønsted acids, such as HF or FSO_3H. Methyl substitution leads to rearranged allylic ions, whereas phenyl substitution gives classical ions with little or no homoaromaticity. Contrary to the claim by Broser and Rahn, phenyl substitution at the C-1, C-3, and C-5 positions of the bicyclo[3.1.0]hexyl skeleton also gave only a classical ion with no trishomoaromatic character. Sauers' claimed trishomocyclopropenylium carboxylic acid **34** was shown to be instead the corresponding protonated starting tricyclic lactone **35**. All attempts to prepare the parent potentially bishomoaromatic 4-cyclopentenyl cation **2a** were unsuccessful. Previously studied 7-norbornenyl and 7-norbornadienyl cations, are, however, indeed of bishomocyclopropenyl ion nature.

Introduction

The concept of homoaromaticity was advanced by Winstein almost 20 years ago.[3] It was found challenging to experimental and theoretical chemists alike.[3,4] The question of homoaromatic overlap has been mainly studied in six π-electron Hückeloid systems,[3] although several two π-electron systems became also known in recent years.[5-8]

The simplest 2π monohomoaromatic cation, the homocyclopropenyl cation **1** and its analogues, were prepared and studied by one of us in preceding work.[7] The parent potentially bishomoaromatic 4-cyclopentenyl cation **2a**, i.e., the bishomocyclopropenyl cation, is still elusive,[9] although bishomoaromaticity in related ethano- and etheno-bridged analogues (i.e., in 7-norbornenyl and 7-norbornadienyl cations **2b** and **2c**) is well documented.[6,29] Winstein's trishomocyclopropenyl cation **3** under stable ion conditions was first prepared by Masamune and co-workers.[5a] Subsequently, several ethano-bridged polycyclic trishomoaromatic cations have also been prepared and studied.[5b,8]

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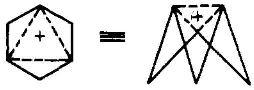
2a



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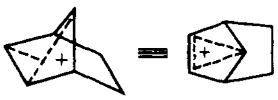

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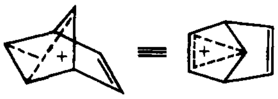
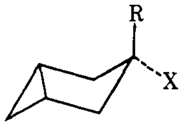


2c

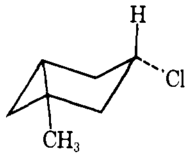
Masamune[5a] was able to prepare ion **3** from bicyclo[3.1.0]hex-3-yl chloride (**4**-Cl) despite previous failure of attempts from the corresponding alcohol.[9] This discrepancy raised controversy and called for further studies. We wish to report now the successful independent preparation of the trishomocyclopropenyl cation **3** from its alcohol precursor, i.e., *cis*-bicyclo[3.1.0]hexan-3-ol **4**-OH, in SbF_5/SO_2ClF solution at −78 °C. The effect of methyl and phenyl substituents on the ionization of bicyclo[3.1.0]hexyl derivatives was also studied. The structures of the claimed 1,3,5-triaryltrishomocyclopropenyl cation **29** of Broser and of the trishomocyclopropenylium carboxylic acid **35** of Sauers were redetermined.[11,14] Attempts to prepare the still elusive potentially bishomoaromatic 4-cyclopentenyl ions are summarized. The structure of the studied ions was elucidated by ^{13}C NMR spectroscopy.

Results and Discussion

Precursor alcohols and chlorides, **4–12**, were prepared by reported methods.[9-14] Bicyclic acid **13** was commercially available.[15] The corresponding carbocations were prepared by ionization of the precursors with superacids, such as FSO_3H, FSO_3H/SbF_5 (1:1), or SbF_5 in SO_2ClF solution at



4, X = OH, Cl
5, R = CH_3, C_6H_5; X = OH



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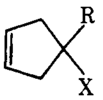
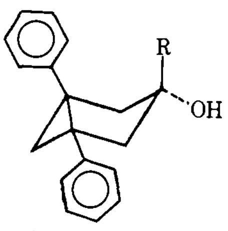
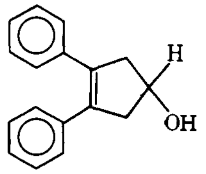


8, R = H; X = Cl, OH
9, R = CH_3, C_6H_5; X = OH



7, R = C_6H_5, H



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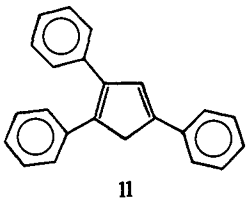

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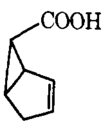

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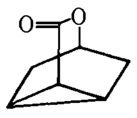

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Table I. ^{13}C NMR Shifts[a] of Observed Carbocations

carbocation	temp of observation, °C	C-1	C-2	C-3	C-4	C-5	C-6	C-7	others
3	−80	4.9, ($J_{C\text{-}H}$ = 195.4 Hz)	7.6 ($J_{C\text{-}H}$ = 168.4 Hz)	4.9	17.6	4.9	17.6		
25	−80	234.5	144.1	222.7	40.5	45.5			CH_3 = 25.1 aromatic: C_i = 132.9, C_o = 136.6, 135.2, C_m = 131.9, 131.4, C_p = 139.7
30	−110	39.5	57.1	262.6	57.1	39.5	23.4		aromatic signals: broad and complex
32	−80	197.8	142.2	197.8	39.6	42.1	39.6		aromatic: peaks at 137.7, 133.6, 131.6, 130.3, 129.4, and 128.1
35[b]	−80	23.3	30.5	13.1	87.9	131.1	30.5	190.0	
33	−80	248.1	128.1	248.1	40.3	31.7	40.3		aromatic: C_i = 139.9, C_p = 130.4, C_o, C_m = 129.6
37-C_6H_5	−110	133.1	133.1	52.2	266.5	52.2			aromatic: C_i = 142.8, C_o = 142.8, C_p = 156.2, C_m = 129.6
38	−110	241.3	149.3	245.2	58.9	58.2			CH_3 = 15.0
43	−80	210.8	147.2	227.9	57.7	54.3			aromatic: peaks at 141.5, 140.5, 140.4, 138.9, 133.8, 132.2, 131.9, 131.0, 129.5, and 127.9
45	−80	213.2		211.5	55.1	49.1			aromatic: complex and broad

[a] Shifts are in parts per million from external capillary Me_4Si. [b] 60-MHz ^{1}H NMR spectrum of protonated lactone exhibited the following shifts (in parts per million from external capillary Me_4Si: 10.95 (s, 1 H), 3.09 and 3.39 (AB_2 patterns, 4 H), 5.94 (m, 1 H), and 2.5 ($(AB)_2$, $J_{H\text{-}H}$ = 14.5 Hz, m, 4 H).

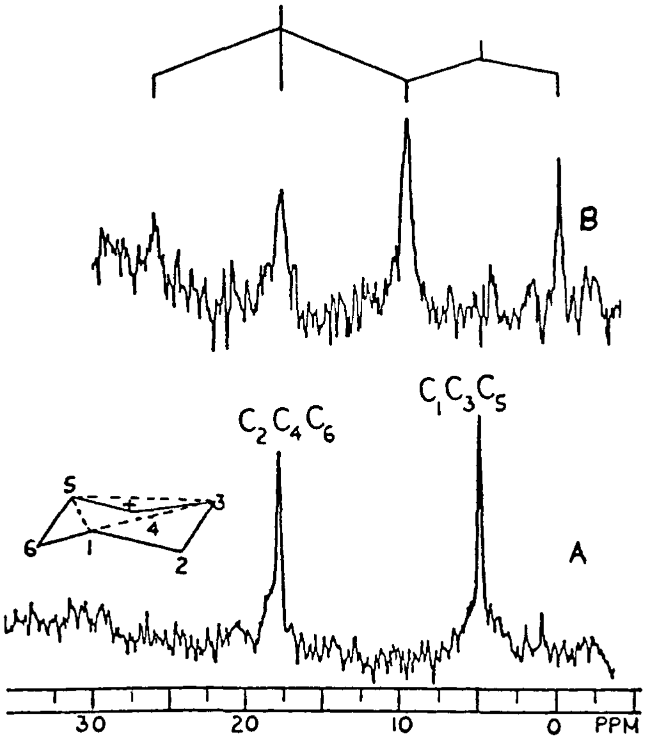
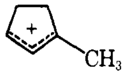


Figure 1. ^{13}C NMR spectra of the trishomocyclopropenyl cation **3** in SbF_5/SO_2ClF solution at −80 °C: A, proton decoupled; B, proton coupled spectrum.

temperatures from −78 to −140 °C. The ^{13}C NMR data of the studied carbocations are summarized in Table I.

Trishomocyclopropenyl Cation 3. In an earlier attempted preparation of ion **3**, the reaction of *cis*-bicyclo[3.1.0]hexan-3-ol **4-OH** with FSO_3H/SbF_5 has been shown to result in formation of the 4-methylcyclopentenyl ion **14**.[9] In contrast, Masamune[5a] showed that cis chloride **2-Cl** gives on treatment with SbF_5/SO_2ClF solution ion **3**.

We have now found that both *cis*- and *trans*-bicyclo[3.1.0]hexan-3-ols **4-OH** and the corresponding chlorides **4-Cl**, upon ionization with FSO_3H/SO_2ClF at −78 °C, give 3-methylcyclopentenyl ion **14**. The cis chloride **4-Cl** with SbF_5/SO_2ClF at −78 °C gives ion **3**, as reported by Masamune, but the trans chloride **4-Cl**, under similar conditions, gives only 3-cyclohexenyl ion **15**. The cis alcohol **4-OH**, however, upon treatment with freshly distilled SbF_5/SO_2ClF at −78 °C, cleanly gives the trishomocyclopropenyl ion **3**. The ^{13}C NMR spectrum (Figure 1) of ion **3** shows no trace of the 3-methylcyclopentenyl ion **14**. Ion **3** was found to be stable up to −20 °C, above which it decomposed to unidentifiable tar.



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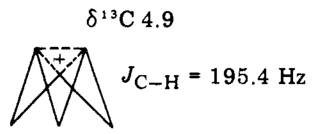
Masamune,[5a] in his studies, suggested that the trishomocyclopropenyl cation **3** may be initially formed from the alcohol precursor in protic acid solutions, but will then rearrange rapidly to the allylic ion. Consequently, we generated ion **3** from both *cis*-**4-OH** and *cis*-**4-Cl** in SbF_5/SO_2ClF solution and then added FSO_3H in sixfold molar excess over the initial concentration of the substrate. No change in the ^{13}C NMR spectrum of ion **3** was observed, and the stability of ion **3** was in no way affected. Similar behavior was observed upon addition of HF. We consider the success of preparing **3** directly from *cis*-**4-OH** to be due to the use of highly purified SbF_5, which is free from protic acid impurities. Previous failure[9,16] is attributed to the proton-initiated opening of the cyclopropyl ring of the bicyclo[3.1.0]hexyl skeleton before ionization. Our results are in accord with Sorensen's[17] view that bicyclo[3.1.0]hexan-3-ols in protic acid media tend to form methylcyclopentenols. Reports of similar contrasting behavior of substrates in conventional acids and superacids have appeared recently.[18,19]

Results obtained in superacidic media show that the behavior of *cis*- and *trans*-bicyclo[3.1.0]hexan-3-yl chlorides **4-Cl** and alcohols **4-OH** closely parallels the solvolytic behavior of the tosylates in that the trishomocyclopropenyl cation **3** can be formed only when σ participation accompanies ionization.

Since Winstein's trishomocyclopropenyl cation **3** has now been obtained from both the alcohol as well as the chloride precursors and once formed has been shown to be stable to protic acids, unequivocal evidence has been obtained for the carbocationic nature of **3**, excluding the possibility of any heteroatom containing ionic species.

The trishomocyclopropenyl cation **3** as shown by the highly shielded ^{13}C NMR shift for the equivalent five-coordinated carbocationic carbons clearly is a nonclassical carbocation. It compares closely with the reported ethano-bridged analogue **16**[5b] and Coates's pentacyclic ion **17**.[8] Large ^{13}C–^{1}H coupling constants of the carbocationic carbons also are indicative of their high s character, typical of nonclassical ions.[20] Similar coupling constants have also been observed in the homocyclopropenyl cation **1**[7] and the bishomoaromatic 7-norbornenyl cation **2b**,[6] although the ^{13}C NMR chemical shifts in these systems are significantly different.



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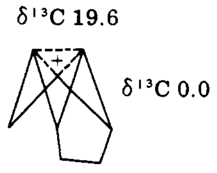

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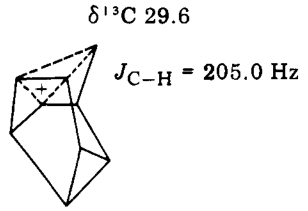

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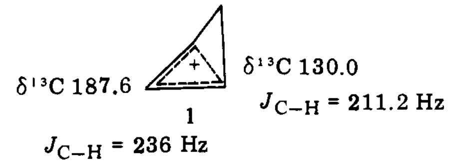

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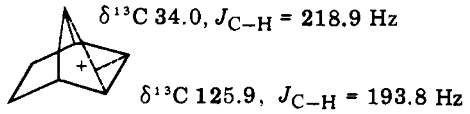
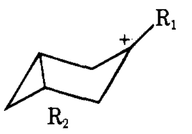


2b

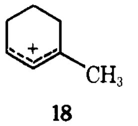
Effect of Methyl and Phenyl Substitution on Bicyclo[3.1.0]-hexyl Systems. In an attempt to prepare substituted trishomocyclopropenyl cations, the ionization of various methyl and phenyl substituted *cis*-bicyclo[3.1.0]hexyl alcohols and chlorides was investigated.

Ionization of the tertiary 3-methyl-*cis*-bicyclo[3.1.0]-hexan-3-ol **5**-CH_3 with SbF_5/SO_2ClF at −80 °C resulted in the formation of the 3-methylcyclohexenyl cation **18**.[9] No evidence for the formation of trishomoaromatic ion **19** or the classical ion **22** was obtained. 1-Methyl-*cis*-bicyclo-[3.1.0]hexan-3-yl chloride (**6**) in SbF_5/SO_2ClF at −90 °C also yielded the 3-methylcyclohexenyl cation **18** as the main product (although small amounts of unidentified byproducts were also present).

In an attempt to prevent the 1,2-hydride shift from taking place, and thus, allylic ion formation, 3-phenyl-*cis*-bicyclo-[3.1.0]hexan-3-ol **5**-C_6H_5 was treated with SbF_5/SO_2ClF solution at −80 °C, but it gave only the 3-methyl-1-phenylcyclopentenyl ion **25**. Thus, the result of interaction of the phenyl-stabilized carbenium center with the cyclopropane ring is the opening of the latter rather than delocalization of charge forming a trishomocyclopropenyl cation **21** (at studied temperatures).



22, $R_1 = CH_3$; $R_2 = H$
23, $R_1 = H$; $R_2 = CH_3$
24, $R_1 = C_6H_5$; $R_2 = H$



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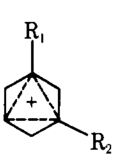
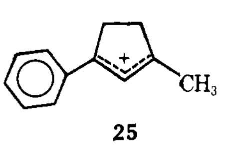


19, $R_1 = CH_3$; $R_2 = H$
20, $R_1 = H$; $R_2 = CH_3$
21, $R_1 = C_6H_5$; $R_2 = H$



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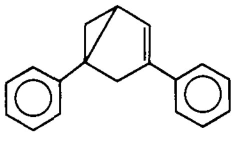
These results are in contrast with the observation of Coates[8] that 9-pentacyclo[4.3.0.0^{2,4}0.^{3,8}0.^{5,7}]nonyl cations,[8] which are rigid structures of trishomoaromatic nature, can be also prepared with methyl and phenyl substituents. The calculations of Jorgensen,[21] while consistent with Coates'[8] and Masamune's[5b] results in rigid systems, indicate that, in the parent system, the classical tertiary carbocation will be formed in preference to the delocalized unsymmetrical trishomocyclopropenyl ion. The reason may be hindrance of the change of the boat to chair conformation necessary to form the delocalized ion.

Aryl Substitution at C_1, C_3 and C_5 Positions. Corey and Uda[13] in their demonstration of the lack of σ participation in the solvolysis of *cis*-3-bicyclo[3.1.0]hexyl *p*-toluenesulfonates, prepared *cis*-1,5-diphenylbicyclo[3.1.0]-3-hexyl *p*-toluenesulfonate and measured its ionization rate with respect to the former compound. They found no rate enhancement with phenyl substitution at the C_1 and C_5 positions, and the main products of acetolysis were rearranged olefins **26** and **27**. They also prepared 1,3,5-triphenyl-*cis*-bicyclo[3.1.0]-hexan-3-ol **7**-C_6H_5 and treated it with acidic reagents, such as boron trifluoride etherate and $SOCl_2$; immediate formation of 1,3,5-triphenylbenzene **28** was observed. No evidence was obtained for the formation of any trishomoaromatic ion **29**. Similar observations were later made by Winstein and Lin.[22]



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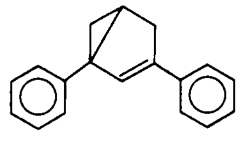

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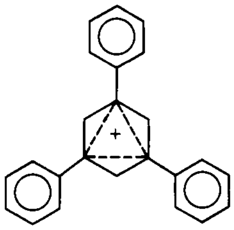

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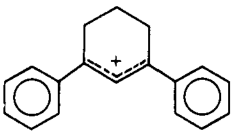
Subsequently, however, Broser and Rahn[14] synthesized a series of 1,5-diphenyl 3-substituted *cis*-bicyclo[3.1.0]hexan-3-ols and carried out UV spectral studies in a variety of acids, such as H_2SO_4, $SbCl_5$, BF_3, and HBr, in CH_2Cl_2 solution. From the observed UV maxima (λ_{max} ~400–500 nm), they claimed to have prepared the 1,3,5-triphenyltrishomocyclopropenyl cation **29**.

To test the obvious discrepancy, *cis*-1,3,5-triphenylbicyclo[3.1.0]hexan-3-ol **7**-C_6H_5 and 1,5-diphenyl-*cis*-bicyclo[3.1.0]hexan-3-ol **7**-H were studied under superacidic conditions. Dissolution of **7**-C_6H_5 in FSO_3H/SO_2ClF solution at −140 °C gave a red-colored solution, whose proton decoupled ^{13}C NMR spectrum indicated the formation of an ion with a carbocation center resonance at $\delta^{13}C$ 262.60. Three resonances in the aliphatic region were observed at $\delta^{13}C$ 57.05, 39.50, and 23.40, respectively. The aromatic resonances were too complex and broad to assign, and the symmetry of the ^{13}C NMR spectrum indicates the exclusive formation of 1,3,5-triphenylbicyclo[3.1.0]hexan-3-yl cation **30**, which is a classical carbocation with little or no trishomoaromatic character. Ion **30** compares closely with the analogous classical 1-phenyl-1-cyclohexyl cation **31**, whose carbocation center is observed at $\delta^{13}C$ 260.0. When the solution was warmed to −70 °C, ion **30** rapidly rearranged to allylic 1,3,5-triphenyl-3-cyclohexenyl cation **32**. The above results are in good agreement with Jorgensen's theoretical calculations.[21] They, however, clearly show that Brosen and Rahn's[14] ion was not of homoaromatic nature. Ionization of 1,5-diphenyl-*cis*-bicyclo[3.1.0]hexan-3-ol **7**-H in FSO_3H/SO_2ClF at −140 or −78 °C gave as the sole product the 1,3-diphenyl-3-cyclohexenyl ion **33** in accordance with the solvolytic studies of Corey[13] and subsequently by Winstein.[10b,22]



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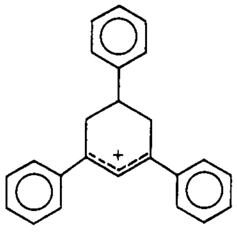

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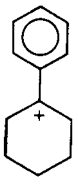

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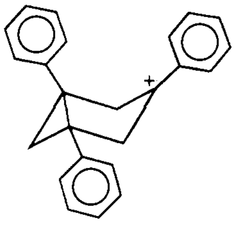

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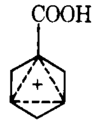
Structure of Sauers' Claimed Trishomocyclopropenylium Carboxylic Acid 34. Sauers[11] claimed, based on ^1H NMR studies, that tricyclic lactone **12**, prepared by the oxidation of 3-nortricyclanone, upon protonation gave trishomocyclopropenylium carboxylic acid **34**. Deno[24] subsequently suggested that structure **35** was more compatible with the obtained ^1H NMR data. The question, however, remained unsettled.



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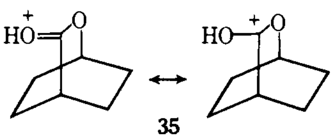

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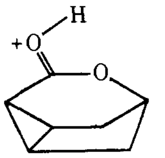
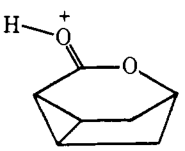
We, therefore, undertook a reinvestigation on the nature of Sauers' ion in superacidic media. When either lactone **12** or bicyclo[3.1.0]hex-2-ene-*endo*-6-carboxylic acid **13** was dissolved in either FSO_3H/SO_2ClF or $FSO_3H/SbF_5/SO_2ClF$ (SO_2) at −78 °C, the resulting solutions showed the same ^1H and ^{13}C NMR spectra.

The ^1H NMR spectrum consists of an $(AB)_2$ pattern centered at 2.5 ppm (J_{H-H} = 14.5 Hz), an AB_2 system (J_{H-H} = 7.0 Hz) centered at 3.09 and 3.39 ppm, a multiplet at 5.94 ppm, and a singlet at 10.95 ppm (in FSO_3/SbF_5). The ^1H NMR data are consistent with the protonated lactone structure **35**. The $(AB)_2$ pattern is assigned to the methylene protons and the AB_2 system to the cyclopropyl protons. The multiplet and low-field singlet are assigned to the bridgehead proton and hydroxylic proton of the protonated carbonyl group, respectively.

In the proton decoupled ^{13}C NMR spectrum, five carbon resonances were observed, consistent with the structure **35**. The cyclopropyl carbons C_1, C_2, and C_6 were observed at $\delta^{13}C$ 23.3 and 30.5, respectively. The methylene carbons C_3 and C_5 and the bridgehead carbon C_4 resonated at $\delta^{13}C$ 31.1 and 87.9, respectively. The carbonyl carbon of the protonated lactone was observed at $\delta^{13}C$ 190.0, also consistent with the O-protonated lactone structure. Protonated lactone **35** can have two conformations, i.e., syn and anti.



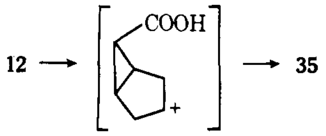
35-*syn*



35-*anti*

The spectra indicate the presence of only one isomeric species, but no differentiation can be made at this time from the available data.

The formation of **35** upon protonation of the bicyclic acid **13** is of interest. Protonation must first take place at the olefinic double bond to give the unstable secondary ion **36**, which then undergoes, through oxygen participation, ring closure. Whether protonation and ring closure take place stepwise or in a concerted fashion cannot be distinguished from our study.



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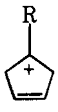
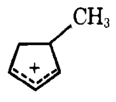
Attempted Preparation of Bishomocyclopropenyl Cations. In the acetolysis of 4-cyclopentenyl bromide, Bartlett and Rice[25] found no anchimeric assistance by the double bond. However, subsequent studies by Hanack,[26] Wiberg,[27] and Allred[28] have indicated such participation. Our earlier studies[9] under superacidic conditions failed to show the formation of bishomocyclopropenyl cations. We have now carried out further studies at very low temperatures (−140 °C) in an attempt to observe bishomocyclopropenyl cations.

Ionization of 4-cyclopentenol or 4-chlorocyclopentene **8**-OH or **8**-Cl with SbF_5/SO_2ClF even at −140 °C gave only 3-cyclopentenyl cation[9] **42**. We found no evidence for the formation of bishomoaromatic ion **2a** or a classical ion **37**-H. The 1,2-hydride shift giving the allylic ion **42** is, thus, obviously extremely fast.



37, R = C_6H_5, CH_3, H



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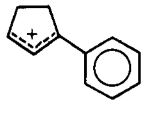

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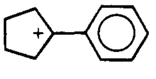

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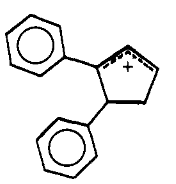
41, R = CH_3, C_6H_5

42

Dissolution of alcohol **9**-CH_3 in SbF_5/SO_2ClF at −140 °C gave a yellow-colored solution. The proton decoupled ^{13}C NMR spectrum of the solution indicated the formation of a mixture of two closely related allylic ions. One of the ions was readily identified as the 3-methyl-3-cyclopentenyl cation **14.** The other ion was assigned, based on the proton noise decoupled ^{13}C NMR spectrum, as the 4-methyl-3-cyclopentenyl ion **38,** a secondary allylic ion. It is interesting to note that 1,2-hydride shift takes place in the tertiary ion **37**-CH_3 to form a secondary allylic ion **38.** By raising the temperature to −60 °C, ion **38** completely rearranges to the tertiary allylic ion **14.**

The phenyl-substituted alcohol **9**-C_6H_5, when treated with SbF_5/SO_2ClF at −140 °C, gave only polymeric material. However, with FSO_3H/SO_2ClF at −140 °C an orange-red solution was obtained. The proton decoupled ^{13}C NMR spectrum of the solution showed the most deshielded peak at δ^{13}C 266.50, followed by olefinic and aromatic absorptions. In the aliphatic region, a single methylene peak was observed at δ^{13}C 52.20. These data clearly indicate the formation of the 4-phenyl-4-cyclopentenyl cation **37**-C_6H_5. Comparing ion **37**-C_6H_5 with the 1-phenyl-1-cyclopentyl cation[23] **41** (carbocationic center at δ^{13}C 268.0) indicates the classical nature of the ion with significant delocalization into the phenyl ring. Thus, ion **37**-C_6H_5 shows little or no bishomoaromatic character. On bringing the solution to −60 °C, the ion rearranges to the 3-phenyl-3-cyclopentenyl ion **39,** together with some unidentified species.

Ionization of 1,2-diphenyl-4-cyclopentenol **10** in FSO_3H/SO_2ClF at −78 or −140 °C resulted only in the formation of diphenylcyclopentenyl cation **43.** In an effort to obtain the symmetrical 1,2,4-triphenyl-4-cyclopentenyl cation **44** (a potential bishomoaromatic ion), we reacted 1,3,4-triphenylcyclopentadiene **11** in FSO_3H/SO_2ClF at −140 °C. However, we observed only exclusive formation of the 1,3,4-triphenyl-3-cyclopentenyl cation **45.**



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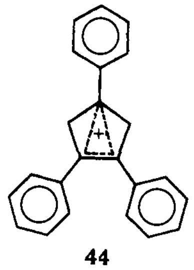

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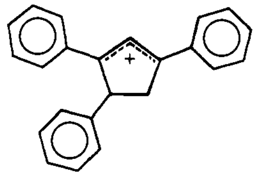

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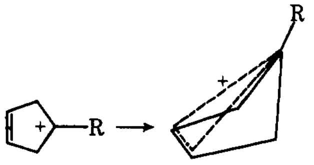
The lack of formation of bishomoaromatic ions from cyclopentyl derivatives may be due to steric reasons. The planar cyclopentene skeleton has to bend into the chair conformation to achieve any significant overlap between the empty p orbital and π-p lobe of the olefinic bond, which is sterically unfavorable. However, when such a conformation already exists, as in the case of 7-norbornenyl and 7-norbornadienyl cations, **2b** and **2c,** bishomoaromatic overlap is, indeed, operative.[6,29]



Experimental Section

All precursors **4–12** were synthesized following literature methods.[9-14] The bicyclic acid **13** was commercially available.[15] 1,3,4-Triphenylcyclopentadiene (**11**) was obtained as the sole product, giving satisfactory spectral and elementary analyses, when 1,2-diphenylcyclopenten-4-one[13] was reacted with phenyllithium or phenylmagnesium bromide in ethereal solution.

Preparation of Ions. Freshly double distilled FSO_3H and SbF_5 were used. The appropriate superacid was dissolved in about twofold amount of SO_2ClF at dry ice/acetone temperature (ca. −78 °C) or while cooled with petroleum ether/liquid nitrogen slush (ca. −140 °C). To this solution was slowly added with vigorous stirring a cooled slurry or solution of the appropriate precursor in SO_2ClF, resulting in an approximately 10–15% solution of the ion.

^{1}H NMR spectra were recorded on a Varian Associates Model A56/60A spectrometer, equipped with variable-temperature probe, and external capillary Me_4Si was used as the reference.

^{13}C NMR spectra were either obtained using a Varian Model XL-100 spectrometer, equipped with FT accessory with a variable-temperature probe, or a Varian Model FT-80 spectrometer, equipped with multinuclei variable-temperature broad-band probe.

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