Stable Carbocations. CLXXXVIII.¹ Bicyclo[3.1.0]hexenyl Cations

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A series of bicyclo[3.1.0]hexenyl and benzobicyclo[3.1.0]hexenyl cations were prepared under stable ion conditions. Based on ¹³C NMR data, these ions are considered to be cyclopentenyl-like cations with charge delocalization into the fused-on cyclopropane ring. They show no homoantiaromatic or Möbius-type character. ¹³C NMR spectra of related cyclohexadienyl cations (benzenium ions) which photochemically rearrange to the corresponding bicyclo[3.1.0]hexenyl cations are also reported for comparison.

Photochemical transformation of cyclohexadienyl cations to bicyclo[3.1.0]hexenyl cations in fluorosulfuric acid– SO₂ (or SO₂ClF) solution at low temperature has received considerable attention.² The reaction was shown to occur largely with retention of configuration.³ Both the parent cyclohexadienyl (1)⁴ and bicyclo[3.1.0]hexadienyl (2)^{2c} cations have recently been prepared and characterized by ¹H



NMR. Although 1 and 2 are structurally related isomeric carbocations, the former has been shown to possess no antiaromatic homocyclopentadienyl cation (3)⁴ nature, and the latter contains a fully formed cyclopropane ring with charge delocalization involving the C_1-C_6 and C_5-C_6 (instead of C_1-C_5) bonds, undergoing stereospecific degenerate circumambulation of the cyclopropane ring about the cyclopentenyl cation system. In contrast, when going from the cyclohexadienyl to the cyclooctatrienyl (4) cation the strong 1,7 overlap in the latter makes the C_7 system homoaromatic.⁵ Neither of the isomeric C_8 cations 4 and 5 were directly observable. Hehre⁶ has suggested that the bi-



cyclo[3.1.0]hexenyl cation could be termed as a $6-\pi$ "Möbius aromatic" system, similar to the homotropylium ion. Both systems have been shown, however, to exhibit geometrical structures consistent with normal Hückeloid type character and Möbius structures are not considered to be of importance.⁷

We have recently reported the ¹³C NMR spectrum of the homotropylium ion 6, showing that the methylene-bridge carbon (C₈) is hardly deshielded, while both C₁ and C₇ bear substantial positive charge.⁸ In contrast, in the bicyclo-[3.1.0]hexenyl cations positive charge should be delocalized through the electron-rich external cyclopropane bonds unto C₆, instead of unto C₁ and C₅. It was, therefore, of great interest to study these systems.

We now report the ¹³C NMR spectroscopic study of the parent and substituted bicyclo[3.1.0]hexenyl cations, showing that, indeed, there is substantial positive charge delocalized unto the methylene-bridge carbons. The structural aspects of the ions were also compared to their corresponding cyclohexadienyl (benzenium) ions.

Interested in the ability of the cyclopropane ring to in-

teract with an adjacent carbocationic center,⁹ and to compare it when competing with a fused-on benzene ring, we also extended our studies to a series of novel benzobicyclo-[3.1.0]hexenyl cations.

Results and Discussion

A. Bicyclo[3.1.0]hexenyl Cations. The parent bicyclo-[3.1.0]hexenyl cation (2) was prepared from 4-methoxybicyclo[3.1.0]hexene in FSO_3H - SbF_5 - SO_2ClF solution at -78°. The ¹H NMR spectrum of the solution of 2 at -78°



was identical with that previously reported.^{2c} The proton noise-decoupled ¹³C NMR spectrum (Figure 1a) consisted of four carbon resonances (in addition to the methyl signal of protonated methanol). Assignments were made with the aid of the proton coupled spectrum (Figure 1b).

It is interesting to compare the 13 C NMR parameters of ion 2 with those of the homotropylium (6)⁸ and cyclopentenyl (7)¹⁰ cations, as shown.



There is a significant difference in carbon shifts for the methylene-bridge carbons in the bicyclo[3.1.0]hexenyl cation 2 and the homotropylium ion 6.8 Likewise, the two bridgehead carbons (C_1 and C_5) in 2 are much less deshielded than the corresponding ones $(C_1 \text{ and } C_7)$ in 6. Undoubtedly, charge delocalization in the former does not substantially involve the internal fused cyclopropane bond (C_1-C_5) , while substantial charge delocalization forming the homoaromatic $6-\pi$ system is evident in the latter. One further notices that the bridge methylene carbon (C_6) in 2 is about 60 ppm downfield from the other cyclopropanering carbons (C_1 and C_5), while the opposite is found in the case of homotropylium ion 6 (C₈ is about 80 ppm upfield from C_1 and C_7). The one-bond ¹³C-H coupling constants for the cyclopropane ring carbons in 2 are substantially larger than the corresponding ones in 6. This also is in



Figure 1. (a) Proton noise-decoupled ¹³C NMR spectrum of the parent bicyclo[3.1.0]hexenyl cation in FSO₃H-SbF₅-SO₂ClF solution at -75° . Carbon resonance at δ ¹³C 62.08 is due to the protonated methanol. (b) Proton-coupled ¹³C NMR spectrum of 1.

agreement with the presence of a cyclopropane ring in $2.^9$ Furthermore, comparison of bicyclic ion 2 and the cyclopentenyl cation 7 indicates that the parent bicyclo-[3.1.0]hexenyl cation, indeed, is best represented as a cyclopentenyl cation with charge delocalization into the fused cyclopropane ring.

Bicyclo[3.1.0] hexenyl cations are known to be also formed photochemically from their corresponding cyclohexadienyl cations.¹¹ We have, therefore, examined the ¹³C NMR spectra of several polymethylated benzenium ions⁴ 8–10 and their photochemically rearranged products 11–13 in FSO₃H–SO₂ClF solution. ¹³C NMR parameters, including the chemical shifts, multiplicities, and coupling constants, are summarized in Table I along with their assignments.

Although carbon shifts cannot be used as a direct measure of charge density, comparison of shift difference among closely related system gives a good indication of the



general trend of charge distribution.¹² For cyclohexadienyl cations, C_1 (and C_5) and C_3 are generally much more deshielded than C_2 (and C_4), indicating that positive charge is heavily delocalized unto C_1 , C_3 , and C_5 positions. This is also shown by the fact that methyl carbons at the C_1 , C_3 , and C_5 positions in these ions are more deshielded than those at C_2 and C_4 positions. In their photochemically rearranged products, 11–13, C_2 and C_4 become more deshielded

Table I ¹³C NMR Parameters of Bicyclo[3.1.0]hexenyl and Cyclohexadienyl Cations (Benzenium Ions) in FSO₃H Solutions at −78°

Ion	C1. C-	C2, C4	с,	C ₆	C1 CH2	C2 CH2	C ₂ CH ₂	Ce CH ₂
·····	- 17 - 5		5	<u> </u>	· · · ·			-03
8	194.25	142.36	175.32	57.90	23.08	17.15		
	(s)	(s)	(d, 162.5)	(t, 117.5)	(q, 130.0)	(q, 12 7.5)		
9	186.39	141.35	192.65	55.08	23.11	14.50	23.11	
	(s)	(s)	(s)	(t, 116.4)	(q, 129 .5)	(q, 128.3)	(q, 129.5)	
10	193.85	139.52	191.85	57.58	23.26	14.50	23.26	20.51
	(s)	(s)	(s)	(d. 134.2)	(a. 129.5)	(a. 128.7)	(q. 129.5)	(q, 129.0)
11	61.31	237.69	137.42	106.52	9.87	22.97		-
	(s)	(s)	(d. 181.9)	(dd, 164.5, 167.6)	(a. 130.4)	(a. 131.0)		
12	59.40	232.74	145.44	105.56	9.56	20.74	8.76	
	(s)	(s) ·	(s)	(dd. 167.9, 176.5)	(a. 130.0)	(a. 130.0)	(a. 128.8)	
13	65.48	228.70	149.08	124.50	11.13	21.48	11.13	8.34
	(s)	(s)	(s)	(d, 161.5)	(q, 130.2)	(q, 129.4)	(q, 130.2)	(q, 130.0)

than C_3 , while both C_1 and C_5 are much more shielded. The bridge cyclopropane-ring carbons (C_6), on the contrary, become more deshielded than their corresponding ones in the precursor cyclohexadienyl cations. C_2 and C_3 in the rearranged ions 11–13 show chemical shifts in the region of those in the allylic cation 7. Again, the methyl carbons in these ions display corresponding effects.

Positive charge, as shown, is substantially delocalized over C₂, C₄, and C₆ in bicyclo[3.1.0]hexenyl cations, which are best represented as cyclopentenyl-type carbenium ions with charge delocalization into the cyclopropane ring. The increase of one-bond $J_{^{13}C-H}$ of C₆ in these ions further substantiates the formation of the cyclopropane ring.

B. Benzobicyclo[3.1.0]hexenyl Cations. The parent secondary ion 14-H and tertiary ions 14-R were prepared from the corresponding alcohols 15 (or ketone 16^{13}) in either FSO₃H-SO₂ClF or FSO₃H-SbF₅ solutions at -78° .



The secondary ion 14-H slowly underwent ring opening to give the naphthalenium ion¹⁴ above -50° , while tertiary ions are more stable.



The complete ¹H and ¹³C NMR parameters for ions 14-R are summarized, with their assignments, in Table II. Assignments, multiplicities, and coupling constants (J_{CH} in hertz) were made with the aid of proton-coupled FT ¹³C NMR spectra. Typical are the spectra shown in Figure 2 for ions 14-R.

The methylene-bridge carbons in the benzobicyclo-[3.1.0]hexenyl cations (C₈) and those (C₆) in bicyclo-[3.1.0]hexenyl cations are substantially more deshielded than the rest of the cyclopropane carbons, indicating



charge delocalization through the external cyclopropyl carbon-carbon bonds (C₁-C₈ and C₇-C₈ in 14-H). C₈ in the





Figure 2. 60-MHz ¹H NMR spectra of benzobicyclo[3.1.0]hexenyl cations at -75° in FSO₃H-SO₂ClF solution.

parent benzobicyclo[3.1.0]hexenyl cation 14-H is about 10 ppm less deshielded than the corresponding C₆ carbon in the parent bicyclo[3.1.0]hexenyl cation, owing to the presence of the fused-on benzene ring in the former so that positive charge is shared by a relatively larger π system.

The benzobicyclo[3.1.0]hexenyl cations could also be considered as cyclopentenyl cation derivatives with charge delocalization into both the cyclopropane and benzene rings. Substitution at C_6 with alkyl groups, from methyl to isopropyl groups, causes graduate deshielding at C_6 and shielding at the cyclopropane ring carbons, while the benzene ring positions do not vary much.

In the parent bicyclo[3.1.0]hexenyl cation 2, $H_{6,exo}$ and $H_{6,endo}$ show different chemical shifts at δ 3.98 and 4.28, respectively.^{2c} The difference between $H_{8,exo}$ and $H_{8,endo}$ in the parent benzobicyclo[3.1.0]hexenyl cation 14-H and its related tertiary ions (Table I) falls in similar order. The smaller chemical shift difference ($\delta_{endo} - \delta_{exo}$) of the methylene-bridge protons (+0.30 ppm in 2 and +0.60 ppm in 14-H) of bicyclo[3.1.0]hexenyl-type cations is in contrast to



H and

	1	4 -H	14	-cH ₃	14-C	Н2СН3	14 -C	:н(сн ₃) ₂	14	P-OH ^b
sition	6 ¹ H	6 ¹³ C	6 ¹ H	1 ³ د	6 ¹ H	6 ¹³ C	6 ¹ H	ه ¹³ د	6 ¹ H	6 ¹³ C
1	5.30	49.2	4.85	49.0	4.74	47.2	4.86	45.0	4.40	30.9
		(d, 183.3)		(d, 186.5)		(d, 187.2)		(d, 185.8)		(d, 184.5)
2	8.15	131.9	8.05	130.8	8.15	130.7	8.16	130.4		129.7
		(d. 169.5)		(d, 169.7)		(d, 169.0)		(d, 169.4)	7.90	(d, 168.7)
e	8.58	139.4	8.42	134.4	8.50	133.8	8.45	132.9		126.5
		(d, 169.9)		(d, 169.3)		(d, 170.5)		(d, 170.4)		(d, 167.9)
4	7.98	127.2	7.95	126.7	7.98	126.7	7.92	126.9	8.52	129.7
		(d. 169.9)		(d, 170.7)		(d, 172.9)		(d, 171.4)		(d, 168.7)
2	8,50	151.9	8.50	149.1	8.49	148.8	8.56	148.3		143.8
		(d, 163.4)		(d, 165.1)		(d, 169.8)		(d, 169.2)		(d, 164.3)
9	10.78	227.1		249.6		255.0		259.0		219.5
,		(d. 183.4)		(s)		(s)		(s)		(s)
7	4.95	50.6	4.64	44.3	4.78	43.9	4.70	43.3	3.82	33.1
		(d, 190.3)		(d, 185.2)		(d, 185.6)		(d, 185.1)		(d, 184.8)
8	3.68, exo	103.5	3.22, exo	89.1	3.28 , exo	89.3	3.26 , exo	89.0	2.85, exo	60.2
	4.28, endo	(dd, 170.2,	3.60 , endo	(dd, 171.7,	3.62 , endo	(dd, 172.0,	3.60, end o	(dd, 171.6,	3.10 , endo	(dd, 171.4
		172.9)		174.4)		172.9)		172.8)		171.5)
6		173.3		169.6		169.3		169.4		163.1
		(s)		(s)		(s)		(s)		(s)
0		142.4		140.3		139.5		139.1		127.7
1		(s)		(s)		(s)		(s)		(s)
μ,			3.48	24.6	1.78	11.8	1.40	20.4		
Î				(a, 131.2)		(q, 131.1)		(q, 129.7)		
						i	1.62	21.7		
								(q, 130.0)		
CH,					3.89	32.5				
4						(t, 129.2)				
CH							4.28	39.7		
								(d. 131.4)		

that $(\delta_{\mathrm{H}_{8,\mathrm{endo}}} - \delta_{\mathrm{H}_{8,\mathrm{exo}}} - 5.8 \mathrm{ppm})$ in the homotropylium ion 6.⁵ This corresponds to the difference in J_{CH} in these three systems indicating that both 14 and 2 are different in nature from 6. The homoaromatic nature of 6 thus causes a substantial ring current effect to shield the H_{8,endo} proton, while the effect is relatively small in charge-delocalized cvclopentenyl type ions 14 and 2. This finding is also in accord with our recent results showing that 1,3-orbital interaction to produce homoaromaticity is more important in smaller cycloalkenyl cations, such as the parent cyclobutenyl cation 17 ($\delta_{H_{4,endo}} - \delta_{H_{4,exo}} - 0.82$)¹⁵. The latter has been shown to be the truly homoaromatic $2-\pi$ system, i.e., the homocyclopropenyl cation.¹⁵

Experimental Section

Materials. 4-Methoxybicyclo[3.1.0]hexene was prepared by direct irradiation of a solution of benzene in methanol at room temperature according to the literature procedure,¹⁶ and purified by GLC

1,1a,6,6a-Tetrahydrocycloprop[a]inden-6-one (16) was prepared from trans-2-phenylcyclopropanecarboxylic acid chloride according to literature procedures,¹³ bp 79-81° (0.4 mm).

1,1a,6,6a-Tetrahydrocycloprop[a]inden-6-ol (15-H) was prepared by reduction of 16 with LiAlH₄ in anhydrous ether in the usual manner: mp 83.5-84.3°; NMR (CDCl₃, capillary Me₄Si) δ 7.78 (4 H, s, aryl H), 6.14 (1 H, d, J = 6.4 Hz, H₆), 2.95 (1 H, m, benzyl H), 2.70 (1 H, s, OH), 2.58 (1 H, m, H7), 1.50 (1 H, m, anti H₈), and 1.04 (1 H, m, syn H₈).

6-Methyl-1,1a,6,6a-tetrahydrocycloprop[a]inden-6-ol (15-CH₃) was prepared from 16 and methylmagnesium bromide in anhydrous ether: mp 47-48°; NMR (CDCl₃, capillary Me₄Si) δ 7.74 (4 H, s, aryl H), 2.94 (1 H, m, benzyl H), 2.40 (1 H, m, H₇), 2.43 (1 H, s, OH), 2.14 (3 H, s, CH₃), 1.58 (1 H, m, anti H₈), and 0.95 (1 H, m, syn H₈).

6-Ethyl-1,1a,6,6a-tetrahydrocycloprop[a]inden-6-ol (15-CH₂-CH₃) was prepared from 16 and ethylmagnesium bromide in anhydrous ether: bp 232–233°; NMR (CDCl₃, capillary Me₄Si) δ 7.66 (4 H, s, aryl H), 2.82 (1 H, m, benzyl H), 2.78 (1 H, s, OH), 2.40 (2 H, CH₂), 2.30 (1 H, m, H₇), 1.42 (1 H, m, anti H₈), 1.36 (3 H, t, CH3), and 0.92 (1 H, m, syn H8).

6-Isopropyl-1,1a,6,6a-tetrahydrocycloprop[a]inden-6-ol [15-CH-(CH₃)₂] was similarly prepared from 16 and isopropylmagnesium bromide in anhydrous ether: bp 197° dec; NMR (CDCl₃, capillary Me₄Si) δ 7.70 (4 H, S, aryl H), 2.90 (1 H, m, benzyl H), 2.44 (1 H, m, H₇), 1.60 (1 H, h, CH), 1.60 (3 H, d, CH₃), 1.30 (3 H, d, CH₃), 1.34 (1 H, m, anti H₈), 0.94 (1 H, m, syn H₈), and 0.60 (1 H, s, OH).

Preparation of Ions. The parent bicyclo[3.1.0]hexenyl cation 2 was prepared by careful addition of 4-methoxybicyclo[3.1.0]hexene in SO₂ClF at -78° to FSO₃H-SO₂ClF solution with stirring. The ion was formed cleanly without any formation of benzenium ion, and it showed similar thermal decomposition at higher temperature as previously described.^{2c}

Methyl-substituted bicyclo[3.1.0]hexenyl cations 11-13 were prepared by irradiation of the solution of their corresponding benzenium ions, which were prepared by addition of methyl-substituted benzene to FSO₃H-SO₂ClF solution at Dry Ice-acetone bath temperature (ca. -78°), at low temperature with a Hanovia 450-W mercury arc lamp. The progress of the reaction was allowed for maximum conversion after about 8-12 hr.

Benzobicyclo[3.1.0]hexenyl cations 14-R were also prepared in a similar way from their corresponding alcohols in either FSO₃H-SO₂ClF or FSO₃H-SbF₅-SO₂ClF solutions at Dry Ice-acetone bath temperature (-78°) .

Proton and Carbon-13 NMR Spectroscopy. ¹H NMR spectra were obtained using Varian Associates Models A56/60A and HA-100 NMR spectrometers, equipped with a variable-temperature probe. Tetramethylsilane was used as reference. ¹³C NMR spectra were obtained using a Varian VFT, XL-100-15 spectrometer equipped with a broad-band proton noise decoupler and a variable-temperature probe. The instrument was operated in the pulse Fourier transform mode. Carbon shifts were measured from the ¹³C signal of capillary Me₄Si (5% enriched).

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Registry No.-2, 32730-99-7; 8, 31426-84-3; 9, 40854-61-3; 10, 27458-89-5; 11, 53966-99-7; 12, 53966-98-6; 13, 52059-03-7; 14-H, 56377-03-8; 14-CH3, 56377-04-9; 14-CH2CH3, 56420-55-4; 14-CH(CH₃)₂, 56377-05-0; 14-OH, 56377-06-1; 15-H, 22228-27-9; 15-CH₃, 56403-16-8; 15-CH₂CH₃, 56403-17-9; 15-CH(CH₃)₂, 56403-18-0; 16, 5771-62-0; methyl bromide, 74-83-9; ethyl bromide, 74-96-4; isopropyl bromide, 75-26-3; 4-methoxybicyclo[3.1.2]hexene, 56377-02-7.

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