STABLE POLYFLUORINATED CYCLOALKENYL CATIONS AND THEIR NMR SPECTRA

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At the present time only a few cases of the formation of long-lived polyfluorinated cations are known [1-3], and they include derivatives of 1,2-substituted perfluorocycloalkenes [4] (scheme 1):



 $\mathbf{R} = \mathbf{F}$, Cl, OCH₃, n = 0, 1, 2, 3.

In the present work we are reporting on the synthesis and ¹³C and ¹⁹F NMR spectra of new polyfluorinated cycloalkenyl cations (IIa) (n = 1, $R = C_2F_5$), (IIb) (n = 2, $R = CF_3$) and (IIc) (n = 3, $R = C_2F_5$), obtained by the action of an excess of antimony pentafluoride (see the experimental section) on the corresponding 1-methoxyperfluoro-2-alkylcycloalkenes (Ia-c).*

The ¹³C NMR spectra of the initial alkenes and of the products from their reaction with antimony pentafluoride were interpreted on the basis of the multiplicity and the chemical shifts (CF) of the signals and also from the characteristic spin—spin coupling constants ${}^{1}J_{13}C_{-19F}$ and ${}^{2}J_{13}C_{-19F}$ [5]. The NMR spectra of the cation (IIb) are given in Fig. 1, as an example. From the spectral parameters given in Table 1 it follows that the signals of C¹, C³, C⁹, and F³ in compounds (IIa-c) lie in the downfield region from (Ia-c). Here, a change in the multiplicity of the C³ signals from triplet to doublet is observed in the transition from (Ia-c) to the products from their reaction with antimony pentafluoride. Thus, the spectral data demonstrate conclusively that long-lived cations (IIa-c) are formed during the treatment of (Ia-c) with antimony pentafluoride. (The NMR spectra do not change when the samples are kept for several months.)

Apart from the direct observation of cations of type (II), which have often been postulated as intermediates in a number of reactions, the distribution of positive charge in them is of some interest. It can be studied best in the ¹³C NMR spectra [6]. As seen from Table 1, the transformation of (Ib, c) into (IIb, c) is accompanied by strong descreening of the C¹, C³, C⁹ nuclei. Here the changes in the chemical shifts ($\Delta \delta = \delta_{cat} - \delta_{olef}$) for (IIb) and (IIc) are 41.9, 69.4, 19.1 and 42.3, 69.9, 22.9, respectively (Table 2). The obtained results and also the practical absence of change in the positions of the other signals and of C², in particular, indicate the formation of cations of the classical allylic type in the case of (IIb, c) (scheme 2).



*The formulas and numbers of the respective atoms are given in Table 1.

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Fig. 2. Variation of the ^{13}C chemical shifts (ô, ppm) of the $C^1-C^2-C^3$ triads in the cations (IIa-e).

Stabilization of the charge at C¹ and C³ is evidently secured by the participation of the electron pairs of the oxygen and fluorine atoms, since the downfield shifts of the C⁹ ($\Delta\delta$ = 19.1 and 22.9 ppm) and F³ ($\Delta\delta$ = 73.3 and 72.2 ppm) signals are considerable during the formation of the cations (IIb, c).

It is known that unfluorinated cyclobutenyl cations differ significantly from the fiveand six-membered structures in the distribution of the positive charge and, accordingly, the spectroscopic behavior [7]. The differences in the spectral parameters of our obtained cation (IIa) are also appreciable. Thus, in the transition from (Ia) to (IIa) a downfield shift is characteristic not only of the C¹ and C³ signals but also of the C² signal ($\Delta\delta \sim 12$ ppm, Table 2), and this gives reason to suppose that the positive charge appears at the central atom of the C¹-C²-C³ triad. Similar downfield shifts of the C² signals in the ¹³C spectra are observed during the formation of the cations (IId) (n = 1, R = F) and (IIe) (n = 1, R = OCH₃) (Table 2), which were previously investigated by ¹⁹F NMR in [8], where the possible stabilization of the charge through 1,3 interaction was indicated (resonance structure G). Our observed downfield shifts of the C² resonance during the formation of the cations (IIa, d, e) can evidently be attributed to 1,3 interaction.

TABLE 1. Spectral Parameters (δ , ¹⁹F, δ , ¹³C, ppm; J_{13C-19}F,

-	Demonster	Position			
Compound	Parameter	1	2	3	
$F \xrightarrow{F}_{F} F \xrightarrow{F}_{F} F \xrightarrow{F}_{F} OCH_{3} (IC)$	δ 19F δ 13C 1 <i>J</i> 2 <i>J</i>	154,3 24,5 t	114,2	29,4 110,5 256,0 t 28,0 t	
F = F = F = F = F = F = F = F = F = F =	δ ¹⁹ F δ ¹³ C ¹ J 2J	156,7 20,8 t	115,3 	29,8 114,2 255,0 t 24,4 t	
$ \begin{array}{c} $	δ ¹⁹ F δ ¹³ C ¹ J ² J	159,9 21,5 t	120,6 	35,0 115,4 263,6 t 19,3 t	
$ \begin{array}{c} F & F \\ F & F \\ F & 4 \\ F & F \\ \end{array} $ (Id)	δ ¹⁹ F δ ¹³ C ¹ <i>J</i> ² <i>J</i>	137,1 23,2 t 4,9 d	67,8 130,6 323,5 d 25,7tt	43,6 ~114,7 274 t 22 t	
$ \begin{array}{c} F & & 8 \\ & OCH_3 \\ F & 4 \\ F & 9 \\ F & F \\ F & OCH_3 \end{array} $ (1e)	δ ¹⁹ F δ ¹³ C ¹ J ² J	132,9 22	132,9 22	36,8 116,1 275 * 25 *	
$F \xrightarrow{F}_{F} \xrightarrow{0}^{7} CF_{2}CF_{3}$ $F \xrightarrow{F}_{F} \xrightarrow{0}^{7} CF_{2}CF_{3}$ $F \xrightarrow{F}_{F} \xrightarrow{0}^{7} CF_{2}CF_{3}$ $F \xrightarrow{0}^{7} CF_{3}CF_{3}$ $F \xrightarrow{0}^{7} CF_{3}CF$	δ ¹⁹ F δ ¹³ C 1 <i>J</i> 2 <i>J</i>	196,6 26,5 t	117,1 28,2 t	47,9 180,4 358,4 d 27,3 t	
$F \xrightarrow{F} F \xrightarrow{g} F$ $F \xrightarrow{g} F$	δ ¹⁹ F δ ¹³ C ¹ J ² J	198,6 28,5 t	120,9 43,3 q	42,4 183,6 368,0 d 28,5 t	
$F \xrightarrow{7} (II a)$ $F \xrightarrow{4} (II a)$	δ ¹⁹ F δ ¹³ C ¹ J ² J	200,8 37,8 t	132,3 35,6 t	-67,1 191,0 410,3 d 26,8 t	
$F \qquad OCH_3 \qquad (II d)$	δ ¹⁹ F δ ¹³ C ¹ J ² J	194,9 26,1 t	22,7 142,5 343,0 d —	-45,5 -43,0 176,8 401,1 d 82,8 d	
$\mathbf{F}_{\mathbf{F}} = \begin{pmatrix} 0_{\mathrm{CH}_3}^8 \\ 0_{\mathrm{CH}_3}^9 \\ 0_{\mathrm{CH}_3}^9 \\ 0_{\mathrm{CH}_3}^9 \end{pmatrix} (\mathbf{11, e})$	δ ¹⁹ F δ ¹³ C ¹ J ² J	 194,0 26,2 t	 147,3 	26,2 t -27,4 -28,3 172,6 390,9 d	

*The barriers were obtained by calculation in the AA'BB'X approx-

Hz) of the Vinyl Ethers	(Ia-e) and	the Catio	ns (IIa-e)
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C or F					- Notes	
4	5	6	7	8	9	
58,0 107,1 267,7 t 24,5 tt	58,0 107,2 267,7 t 25,8 tt	37,4 108,9 260,9 t 28,5 t	33,7 111,4 262,2 t 42,1 q	7,2 118,3 286,7 q 36,4 t	59,7	
53,5 109,8 272,5 t 24,4 tt	37,2 112,4 263,1 t 25,4 t		- - - -	-17,9 119,6 271,7 q -	58,8	
40,2 116,6 288,6 t 23,9t			36,0 108,3 253,8t 38,4 9	8,8 117,9 284,8 q 34,1 t	62,4 _	
40,9 ~114,7 274 t 22 t					58,7	°J _{C1−F} ₀==18,3 t
36,8 116,1 275 * 25 *			-	57,7	57,7	
36,6 105,1 261,7 t 29,5 dt	54,7 104,3 254,3t 26,8 tt	41,6 105,4 275,1 t 28,2 t	34,0 108,9 267,1 t 44,3 q	6,6 116,3 284,6 q 33,6 t	82,2 	³ J _{C¹-F³} ==18,8 d J _{F³-F⁷} ==30,9
42,7 106,3 291,5 t 23,8 dt	39,9 106,5 299,5 t 29,9 t			– 17,1 114,9 277,3 q –	77,9	${}^{3J_{C_{1}-F^{3}}=12.9}d_{J_{F^{3}-F^{6}}=12.6}J_{F^{3}-F^{4}}=18.2}$
20,2 116,1 298,9 t 22,0d			37,8 104,5 261,1 t 43,9 q	6,6 115,6 284,3 q 32,9 t	77,2	${}^{3}J_{C^{1}-F^{3}}=25.6 d$ ${}^{3}J_{C^{2}-F^{4}}=11.6 t$
28,0 21,8 112,3 289,2t 65,0 d		-		-	75,3 74,9	⁹ <i>J</i> _{C²−F⁴} =18,1 t ³ <i>J</i> _{C¹−F³} =34,9 d
25,4 18,0 113,1 286,3 t		-		 65,5 	 72,4 71,9 	${}^{3}J_{C1-F^{3}}=45 d$ ${}^{3}J_{C^{2}-F^{4}}=13,5 t$

imation (the X part of the ^{13}C spectrum) to a mean-square error of 1 Hz.



Figure 2 shows the variation in the chemical shifts of the C^1-C^3 carbons in the series of polyfluorinated cyclic cations (IIa-e). It is seen that in the case of the butenyl cations (IIa, d, e) the approach of the C^1 , C^2 , and C^3 signals is due to the increase in C^2 and the decrease in C^1 and C^3 . Here the closest approach of the signals for the $C^1-C^2-C^3$ triad is typical of (IIe), in which the C^2 atom contains an OCH₃ substituent possessing the strongest capacity for stabilization of the positive charge by the opposite delivery of electron density. Consequently, the change in the spectral parameters in the series of cations themselves does not contradict 1,3 interaction in the polyfluorocyclobutenyl cations and particularly in the case of (IIe). This agrees well with the results in [7], where it was shown for the case of unfluorinated cyclobutenyl cations that the degree of 1,3 interaction increases with increase in the capacity of the C^2 substituent to stabilize the charge.

During discussion of the structure of the cations (IIa), d, e) it is necessary to emphasize the following factors: 1) The difference in the chemical shifts $\Delta\delta C^2 = \delta C_{cat}^2 - \delta C_{olef}^2$ for the cations (IIa, d, e) compared with $\Delta\delta C^1$ and $\Delta\delta C^3$ is small and depends little on the nature of the substituent (Table 2); 2) in the ¹³C NMR spectra of the cation (IIe) there is evidence which favors conjugation in the OCH₃ group at the C¹ atom (the OCH₃ group appears in the form of two singlets with equal intensities, which indicates restricted rotation about the C¹==- δ^+ bond) but not in the OCH₃ group at C² (a singlet, which indicates free rotation about the C²=- \overline{O} - bond at least on the ¹³C NMR timescale); 3) for the unfluorinated cyclobutenyl cation [7] the C² signal is observed in the downfield region in relation to C^{1,3} $\delta C^{1,3}$ - δC^2 =-54.1 ppm), which cannot be said of the cations (IIa, d, e) (Fig. 2). In view of the foregoing it can be concluded that the data obtained in the present work make it possible to consider 1, 3 interaction only as an additional possibility for stabilization of the positive charge in polyfluorine-containing cyclobutenyl cations.

In conclusion, it is necessary to emphasize the abnormally large values of the direct spin-spin coupling constants ${}^{1}J_{C-F}$ in the series (IIa, d, e), which are equal to 390-410 Hz (Table 3) against the previously recorded 320-370 Hz (Table 3) against the previously recorded ${}^{3}-F$ [2, 3, 5, 9]. As seen from Table 3, the increase of the constant in the $C^{3}-F$ fragment in this series of cations is accompanied by an increase in the chemical shift of the nuclei of the given fragment. This evidently gives reason to suppose that the change in the ${}^{1}J$ value in the series of cations of one type is due largely to change in the Fermi contact contribution, and this does not contradict the published data [9].

EXPERIMENTAL

The ¹³C-{¹H} NMR spectra were obtained on a Bruker WP-200 SY spectrometer at 50.31 MHz; the length of the main pulse was 8 μ sec (~40°C) and the overall relaxation delay (AQ + PD) was 2 sec at ~25°C. In all cases the sweep was 10 kHz, and the memory in the spectrum was 16K. In individual cases mathematical narrowing of the line was employed. The ¹⁹F NMR spectra were obtained on a Perkin-Elmer R-32 spectrometer at 84.6 MHz. The chemical shifts were determined with reference to TMS and trifluoroacetic acid as external standard.

<u>1-Methoxyperfluoro-2-ethylcyclobutene (Ia)</u>. To 26.2 g (0.1 mole) of perfluoro-1-ethylcyclobutene, while stirring, we added dropwise a mixture of 6.4 g (0.2 mole) of methanol and 0.3 g (0.003 mole) of triethylamine at 0°C. After 1 h the mixture was treated with water and dried with magnesium sulfate. We obtained 21.4 g (78%) of (Ia); bp 109°C. IR spectrum (ν , cm⁻¹): 1692, 1710 (C=C). Found, %: C 30.98; H 1.02; F 62.63. C₇H₃F₉O. Calculated, %: C 30.66; H 1.09; F 62.41.

<u>1-Methoxyperfluoro-2-methylcyclopentene (Ib)</u>. Similarly, from 26.2 g (0.1 mole) of perfluoro-1-methylcyclopentene we obtained 22.3 g (81%) of (Ib); bp 112°C. IR spectrum: 1682 cm⁻¹ (C=C). Found, %: C 30.52; H 0.99; F 62.84. C₇H₃F₉O. Calculated, %: C 30.66; H 1.09; F 62.41.

TABLE 2. Change of the Difference in Chemical Shifts $\Delta \delta = \delta_{cat} - \delta_{olef}$ in the Series of Polyfluorinated Monoalkenyl Cations, ppm

	Δ٥				
Compound	Cı	C²	C3	C°	
(IIc) (IIb) (IIa) (IId)	42,3 41,9 40,9 57,8	2,9 5,6 11,7 11,9	69,9 69,4 75,6 62,1	22,9 19,1 14,8 16,2 *	
(IIe)	61,1	14,4	56,5	10,6 14,4 * 14,9	

*For the two conformers with respect to the $C^1 \bullet \bullet \bullet \hat{O}^+$ bond.

TABLE 3. Change in the Spectral Parameters of the Polyfluorinated Cyclobutenyl Cations (IIa, d, e)

Compound	¹ J _{C³} F, Нг	ôC³, ppm	ôF³*. ppm
(IIa) (IId)	410,0 401,1	191 176,8	-67,1 -45,5
(IIe)	390,9	172,6	-43,0 -28,3 -27,4

*The minus sign corresponds to a downfield shift.

[†]For the two conformers with respect to the $C^1 \cdot \cdot \cdot \delta^+$.

<u>1-Methoxyperfluoro-2-ethylcyclohexene (Ic)</u>. Similarly, from 36.2 g (0.1 mole) of perfluoro-1-ethylcyclohexane we obtained 28.4 g (76%) of (Ic); bp 134°C. IR spectrum: 1647 cm⁻¹ (C=C). Found, %: C 28.86; H 0.88; F 65.96. C_ $H_3F_{13}O$. Calculated, %: C 28.88; H 0.88; F 66.04.

<u>Preparation of the Methoxy-Containing Polyfluorinated Cyclocarbocations.</u> To 0.3 g (0.001 mole) of the 1-methoxyperfluoro-2-alkylcycloalkene, while stirring at 0°C, we added dropwise 0.6 g (0.003 mole) of antimony pentafluoride. The mixture was sealed in a tube.

CONCLUSIONS

1. New stable 1-methoxyperfluoro-2-ethylcyclobutenyl, 1-methoxyperfluoro-2-methylcyclopentenyl, and 1-methoxyperfluoro-2-ethylcyclohexenyl cations were obtained by the action of antimony pentafluoride on the corresponding olefins.

2. The distribution of the charges in the investigated polyfluorinated cycloalkenyl cations was investigated by ¹³C NMR method.

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