Carbocationic Rearrangements of 6b,7,8,8a-Tetramethyl-6b,8a-dihydrocyclobut[*a*]acenaphthylene: Effect of Medium Acidity

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Abstract—Rearrangements of 6b,7,8,8a-tetramethyl-6b,8a-dihydrocyclobut[a]acenaphthylene in acids were investigated by NMR spectroscopy. The initially formed 3b,4-*exo*,4a,5-tetramethyl-3b,4,4a,5-tetrahydro-4*H*-cyclopropa[*a*]phenalen-5-yl cation and its *endo*-epimer rearranged into carbocations of phenalenyl type. Therewith the direction and the rate of rearrangement sharply changed at relatively small variations in the medium acidity.

6b,7,8,8a-Tetramethyl-6b,8a-dihydrocyclobut[*a*]-acenaphthylene (**I**) in superacid media at low temperature transformed into a mixture of two long-lived carbocations: 3b,4-*exo*,4a,5-tetramethyl-3b,4,4a,5-tetra-hydro-4*H*-cyclopropa[*a*]phenalen-5-yl cation (**IIa**) and its *endo*-epimer **IIb** [2] (Scheme 1).

These cations alongside a fast degenerate rearrangement (Scheme 2) [2, 3] suffer slower non-degenerate rearrangements [1] (cf. [2]) whose proceeding according to the preliminary data [1] are essentially affected by the characteristics of the acid environment.

Scheme 3.

Scheme 1.

Scheme 2.

R¹ = Me, R² = H (**a**); R¹ = H, R² = Me (**b**).
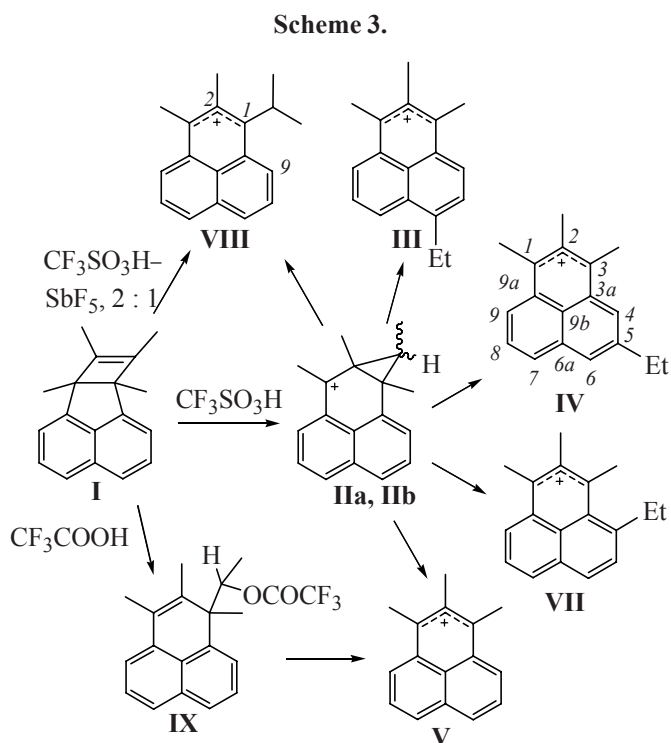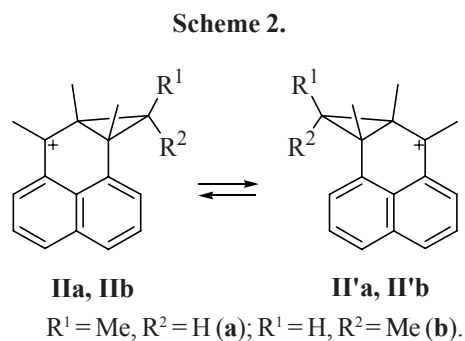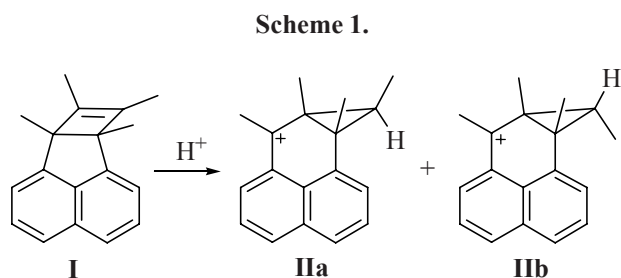
* For preliminary communication, see [1].

Table 1. Chemical shifts in ^{1}H NMR spectra (δ, ppm), calculated values are in brackets

Comp.	H^4	H^5	H^6	H^7	H^8	H^9	1-CH$_3$	2-CH$_3$	3-CH$_3$	Others
III	9.35 d (J 8.4 Hz) [9.28]	8.16 d (J 8.4 Hz) [8.27]		9.31 d.d (J 8.0, 0.8 Hz) [9.32]	8.30 t (J 8.0 Hz) [8.50]	9.42 d.d (J 8.0, 0.8 Hz) [9.45]	3.23 s [3.16]	2.71 s [2.66]	3.23 s [3.13]	3.64 q (Et, J 7.6 Hz), 1.60 t (J 7.6 Hz) [3.67, 1.63 resp.]
IV	9.20 d (J 1.7 Hz) [9.33]		8.77 d (J 1.7 Hz) [8.75]	8.90 d.d (J 7.8, 1.1 Hz) [8.90]	8.22 t (J 7.9 Hz) [8.51]	9.33 d.d (J 8.1, 1.1 Hz) [9.45]	3.18 s^a [3.18]	2.66 s [2.69]	3.21 s^a [3.21]	3.11 q.t (Et, J 7.6, 0.6 Hz), 1.47 t (J 7.6 Hz) [3.20, 1.46 resp.]
V	9.53 d (J 8.0 Hz) [9.52]	8.33 t (J 7.9 Hz) [8.56]	9.01 d (J 7.7 Hz) [8.99]	9.01 d (J 7.7 Hz) [8.99]	8.33 t (J 7.9 Hz) [8.56]	9.53 d (J 8.0 Hz) [9.52]	3.35 [3.22]	2.84 s [2.71]	3.35 s [3.22]	
VI	7.43–7.35 m		7.65 d.d (J 7.4, 1.7 Hz)	7.60 d^a (J 7.4 Hz)	7.49 t (J 7.7 Hz)	7.73 d^a (J 8.0 Hz)	1.73 s	2.14 s^b	2.04 s^b	5.29 q (1-CH, J 6.2 Hz), 0.88 d (1-CCH$_3$, J 6.2 Hz)
VII		8.33 d (J 8.3 Hz) [8.72]	8.88 d (J 8.3 Hz) [8.79]	8.95 d.d (J 7.7, 1.2 Hz) [8.88]	8.29 t (J 7.9 Hz) [8.49]	9.47 d.d (J 8.1, 1.2 Hz) [9.47]	3.30 s^a [3.14]	2.83 s [2.73]	3.36 s^a [3.16]	3.73 q (Et, J 7.4 Hz), 1.75 t (J 7.4 Hz) [3.74, 1.69 resp.]
VIII	9.45 d (J 8 Hz)	8.23 t^a (J 8 Hz)	8.93 d^b (J 8 Hz)	8.90 d^b (J 8 Hz)	8.22 t^a (J 8 Hz)	9.63 d (J 8 Hz)		2.76 s	3.23 s	4.37 septet (i-Pr, J 7 Hz), 1.80 d (J 7 Hz)
VIIIa	[9.45]	[8.50]	[8.91]	[8.88]	[8.44]	[9.89]		[2.71]	[3.21]	[4.18, 1.91 resp.]
VIIIb	[9.50]	[8.53]	[8.96]	[8.94]	[8.52]	[9.54]		[2.80]	[3.15]	[4.73, 1.80 resp.]
IX	7.55 d.d (J 7.3, 1.4 Hz) [7.56]	7.49 d.d (J 8.1, 7.3 Hz) [7.60]	7.73 d.d (J 8.1, 1.4 Hz) [7.74]	7.82 d.d^a (J 8.2, 1.2 Hz) [7.80]	7.63 d.d (J 7.5, 8.2 Hz) [7.72]	7.89 d.d^a (J 7.5, 1.2 Hz) [7.90]	1.83 s [1.48]	2.33 q^b (J 0.9 Hz) [2.31]	2.23 q^b (J 0.9 Hz) [2.24]	5.71 q (1-CH, J 6.4 Hz), 0.96 d (1-CCH$_3$, J 6.4 Hz) [5.91, 0.73 resp.]

^{a,b} These values probably should be exchanged within the same line

This research is aimed at investigation of these non-degenerate rearrangements.

Cations **IIa** and **IIb** generated from hydrocarbon **I** in the acid system CF$_3$SO$_3$H–CDCl$_3$ (molar ratio acid : hydrocarbon **I** 6:1) are relatively stable at room temperature, but the keeping of their solution for 24 h results in their virtually complete conversion into 1,2,3-trimethyl-6-ethylphenalenyl cation (**III**) (Scheme 3).

The structure of this cation was established by the methods of 2D NMR spectroscopy [correlations ^{1}H-^{1}H (COSY) and ^{1}H-^{13}C (HETCOR, COLOC)]. The NMR spectra of cation **III** and other cations are compiled in Tables 1, 2.

The decrease in the amount of CF$_3$SO$_3$H till the molar ratio acid:hydrocarbon **I** was 2:1 led to the formation as the main product (83%) of 1,2,3-trimethyl-5-ethyl-phenalenyl cation (**IV**). Its structure was established from the NMR data: The ^{13}C NMR spectrum contained only two downfield singlets, δ 166.8 and 166.5 ppm, and the ^{1}H NMR spectrum, two doublets, δ 9.20 and 8.77 ppm, with a characteristic "*meta*" coupling constant 1.7 Hz indicating the presence of a substituent in the position *5*. The additional triplet splitting (J 0.6 Hz) of a quartet (δ 3.11 ppm, CH$_2$CH$_3$) showed that this substituent was an ethyl group. A minor reaction product was 1,2,3-trimethyl-phenalenyl cation (**V**) (14%). Its presumed structure [4] was confirmed by comparison of its ^{1}H and

Table 2. Chemical shifts in ^{13}C NMR spectra (δ, ppm), calculated values are in brackets

	C^1	C^2	C^3	C^{3a}	C^4	C^5	C^6	C^{6a}	C^7	C^8	C^9	C^{9a}	C^{9b}	1-CH$_3$	2-CH$_3$	3-CH$_3$	Others
III	164.9 [164.4]	141.9 [146.0]	166.7 [165.5]	129.3 [129.4]	146.9 [142.8]	131.3 [133.3]	169.6 [173.7]	130.5 [131.1]	143.5 [142.1]	130.2 [130.8]	145.4 [142.6]	131.0 [131.2]	123.1 [123.7]	18.5 [16.1]	16.6 [14.3]	18.6 [16.1]	Et 27.8 (CH$_2$), 16.6 (CH$_3$) [32.2, 19.4 resp.]
IV	166.8^a [166.1]	142.4 [146.8]	166.5^a [165.9]	130.4^b [130.8]	146.9^c [145.2]	147.6 [153.9]	148.9^c [149.2]	131.8^b [133.3]	148.5^c [148.4]	130.7 [131.7]	146.0 [143.1]	130.0^b [130.3]	118.3 [121.2]	19.4^d [16.3]	14.9 [14.3]	19.3^d [16.4]	Et 28.4 (CH$_2$), 17.2 (CH$_3$)^d [32.6, 15.1 resp.]
V	169.2 [167.2]	144.3 [147.3]	169.2 [167.2]	131.8 [130.6]	147.8 [144.2]	131.8 [132.0]	150.6 [149.3]	133.2 [132.9]	150.6 [149.3]	131.8 [132.0]	147.8 [144.2]	131.8 [130.6]	123.6 [122.8]	19.3 [16.7]	17.1 [14.4]	19.3 [16.7]	
VII	164.9^a [162.1]	145.2 [147.9]	169.7^a [166.6]	133.4^b [133.5]	173.6 [172.5]	135.3 [131.6]	148.6^c [146.2]	131.8^b [131.2]	148.9^c [147.7]	130.6 [130.7]	145.6 [142.6]	131.7^b [130.1]	124.8 [123.7]	18.8^d [15.4]	17.5^d [15.3]	26.1 [25.8]	Et 33.7 (CH$_2$), 16.9 (CH$_3$)^d [37.5, 8.5 resp.]
VIII^a	177.8	143.0	169.6	130.1^a	146.8^b	130.6^c	149.8^b	132.5^a	149.1^b	130.2^c	147.2^b	130.9^a	123.2	–	16.9	18.5	i-Pr 33.4 (CH), 23.6 (CH$_3$)
IX	49.7 [53.8]	134.6^a [138.3]	130.8^b [131.8]	133.8^a [132.0]	121.2 [116.9]	127.3^c [124.7]	128.2^c [125.6]	134^c [133.1]	128.3^c [125.7]	127.3^c [123.9]	127.1^c [123.6]	138^a [141.1]	129.9^b [126.7]	25.9 [22.4]	16.4^d [13.6]	15.9^d [10.1]	83.9 (1-CH), 15.1 (1-C$\underline{C}$H$_3$)^d, 161.4 q (J_{C-F} 43 Hz), 116.4 q (J_{C-F} 285 Hz) [88.9, 9.8, 154.4, 121.7 resp.]

^{a,b,c,d} These values probably should be exchanged within the same line. ^{e} Calculated values for cation **VIII** are presented in Scheme 4.

^{13}C NMR spectra with the spectra of cation **III**. Another consequence of the reduction in the acid quantity was the sharp acceleration of the reaction: Cations **IIa** and **IIb** we were able to observe only at low temperature. At –48°C alongside cations **IIa** and **IIb** in the reaction mixture a compound is present whose ^{1}H NMR spectrum (Table 1) resembled the spectrum of trifluoroacetate **IX** (see below); it was evidently the corresponding triflate **VI** (molar fraction 12%). Its signals disappeared at warming the solution to –15°C, and therewith became visible the conversion of cations **IIa** and **IIb** into the mixture of ions **IV** and **V**. The latter process completed at heating the sample to –5°C and maintaining it at this temperature for 1.5 h.

The reasons of this sharp change in the reaction direction at relatively small variations in the composition of the medium are not yet clear.

Cations **IIa** and **IIb** generated from hydrocarbon **I** in neat CF_3SO_3H (undiluted by $CDCl_3$) (molar ratio acid:hydrocarbon I 33:1) are quite stable at room temperature, but on keeping the solution for 24 h they practically completely convert into a mixture of cations **III** (11%), 1,2,3-trimethyl-4-ethylphenalenyl (**VII**) (51%), and 1-iso[ropyl-2,3-dimethylphenalenyl (**VIII**) (34%, see below). The structure of cation **VII** was identified by comparison of its ^{1}H and ^{13}C NMR spectra with those of cations **III** and **IV**.

In going from CF_3SO_3H to stronger acid system CF_3SO_3H–SbF_5 (molar ratio 2:1) the reaction selectivity sharply increased: Cation **VIII** formed as the only product (Scheme 3) in a nearly quantitative yield. The structure of this cation was established from the comparison of its ^{1}H and ^{13}C NMR spectra with those of the related cations **III–V,** and **VII**.

In the ^{13}C NMR spectrum of cation **VIII** the signals of atom C^9, CH$_3$ group of the isopropyl fragment, and

of the 2-CH$_3$ group [δ 147.2 (doublet), 23.6 (quartet of double intensity), and 16.9 (quartet) respectively] are considerably broadened: Their half-widths equal 4, 18, and 4 Hz respectively, whereas the half-width of the other signals does not exceed 2 Hz. The calculation by DFT method indicates that the reason of this broadening is the hampered rotation of the isopropyl group leading to the interconversion of two conformers of cation **VIII** (Scheme 4). According to the calculations the stability of conformers **VIIIa** and **VIIIb** is practically the same (the first one is more stable by only 2 kJ mol^{-1}), but the energy barrier in the process (**VIIIa**) → (**VIIIb**) equals 45 kJ mol^{-1}. The broadening of NMR signals under the conditions of fast exchange is proportional to the square of the difference between the chemical shifts of the exchanging nuclei, therefore the largest broadening should be observed for the signals of atom C^9 (the calculated difference between the chemical shifts 2.6 ppm), CH$_3$ group of the isopropyl fragment (6.8 ppm), and for the 2-CH$_3$ group (2.5 ppm) (Scheme 4, the numbers are the chemical shifts difference in the ^{13}C NMR spectrum). This reasoning is consistent with the observed broadening pattern. The value of the energy barrier in the process (**VIIIa**) → (**VIIIb**) estimated from the experimental half-width of the signal of the methyl groups from the isopropyl fragment and the calculated difference between the chemical shifts of these groups in conformers **VIIIa** and **VIIIb** taking into account the occupancy of the conformations equals 46 kJ mol^{-1}, a very close value to the calculated figure for the energy barrier.

A sharp decrease in the medium acidity in going to CF_3COOH leads to the formation of 1-(1,2,3-trimethyl-1H-phenalen-1-yl)ethyl trifluoroacetate (**IX**) (95%) (Scheme 3). Its structure was confirmed by ^{1}H, ^{13}C NMR (Table 1, 2), and mass spectra. The neutral character of the formed compound is proved by the range of the chemical shifts of the protons from the aromatic rings (7.5–7.9 ppm) quite unlike the analogous range characteristic of phenalenyl cations (8.2–9.6 ppm). Besides in the ^{13}C NMR spectrum of the solution the additionsl signals of the trifluoroacetyl group were observed (Table 2). The keeping trifluoroacetate **IX** solution for 2 weeks at room temperature led to its total conversion into cation **V** (40%) and intractable oligomeric impurities.

For the assignment of the NMR signals of phenalenyl cation and acid esters (Tables 1, 2) we used the information on the multiplicity and intensity of the signals and also the comparison with the calculated chemical shifts.

Scheme 4.

VIIIa   VIIIb
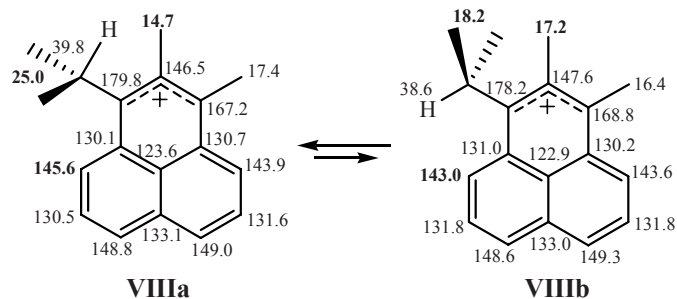
It was shown by examples of cations **IIa** and **IIb** whose ^{1}H and ^{13}C NMR signals had been precisely assigned in [5], and also of cation **III**, that the calculation reproduced well the NMR spectra (see the figure): The mean-square deviations of the calculated chemical shifts were 2.4 ppm for ^{13}C NMR and 0.17 ppm for ^{1}H NMR spectra.

Comparison of experimental and calculated chemical shifts for cations **III, IIa**, and **IIb**.

The discovered rearrangements are fairly unexpected and manifest the rich synthetic potential of the chemistry of long-lived carbocations. The variation of the medium affects the direction of rearrangements, and a great selectivity of the process is observed. We plan to study the mechanism and to establish the reasons of the dependences of the discovered rearrangements on the acidity of the medium.
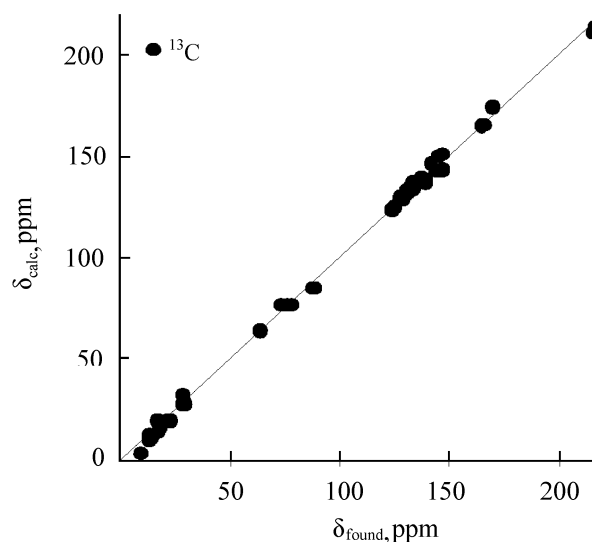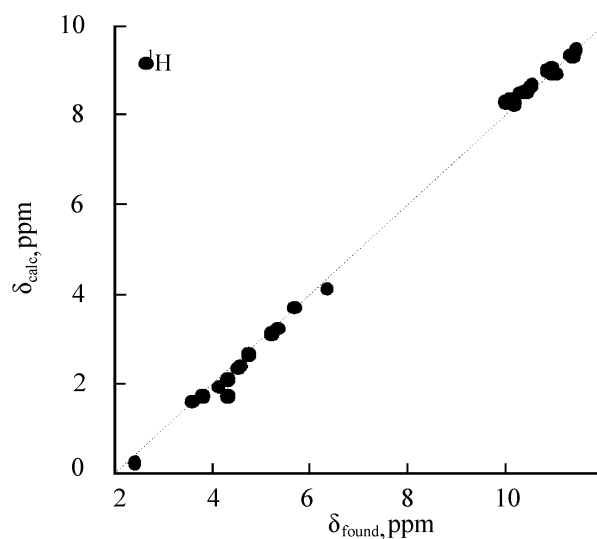
EXPERIMENTAL

The generation of carbocations was performed with the use of CF_3SO_3H purchased from Aldrich, distilled CF_3COOH of "pure" grade (bp 72–73°C), double distilled HSO_3F (bp 158–161°C), $CDCl_3$ and CD_2Cl_2 dried with molecular sieves 4 Å.

NMR spectra (Tables 1, 2) were registered on spectrometers Bruker AM-400 and DRX-500. The tempeature in the probe of the spectrometers was calibrated using a standard methanol sample (–90...50°C) and by the melting points of pentane (–130°C) and naphthalene (80°C). For the intermediate temperatures the interpolation was employed. The mass spectrum of trifluoroacetate **IX** was recorded on a high resolution mass spectrometer Thermo Scientific DFS.

Quantum-chemical calculations of the geometry and the energy of carbocations were performed by DFT method (potential PBE [6]) by "Priroda" program [7] {basis L2 (Λ02, cc-pVTZ) [8], (8s4p2d)/[3s2p1d] for H, (12s8p4d2f)/[4s3p2d1f] for C}. The chemical shifts were calculated by procedure GIAO/PBE/L2 ("Priroda" program), the shielding constants σ were recalculated into the δ scale using for the values of the standard (δ 0 ppm) σ_C 175.78 and σ_H 31.148 ppm

1,2,3-Trimethyl-6-ethylphenalenyl cation (III) [5]. A solution of 80 mg of 6b,7,8,8a-tetramethyl-6b,8a-dihydrocyclobut[*a*]-acenaphthylene (**I**) in 0.2 ml of $CDCl_3$ was added at stirring to 0.2 ml CF_3SO_3H at 0°C, the mixture was kept for 24 h at room temperature, and then the ^{1}H and ^{13}C NMR spectra were registered. The degree

Comparison of experimental and calculated chemical shifts for cations **III, IIa**, and **IIb**.

of conversion of compound **I** into cation **III** was 93%.

1,2,3-Trimethyl-5-ethylphenalenyl cation (IV). A solution of 20 mg of compound **I** in 0.5 ml of $CDCl_3$ was added at stirring to 30 mg CF_3SO_3H at 0°C, and at room temperature the ^{1}H and ^{13}C NMR spectra were registered. The degree of conversion of compound **I** into cation **IV** was 83%.

1,2,3-Trimethyl-4-ethylphenalenyl cation (VII). 40 mg of compound **I** was added at stirring to 0.5 ml CF_3SO_3H at 0°C, the mixture was kept for 24 h at room temperature, and then the ^{1}H and ^{13}C NMR spectra were registered. The degree of conversion of compound **I** into cation **VII** was 51%.

1-Isopropyl-2,3-dimethylphenalenyl cation (VIII). 45 mg of compound **I** was added at stirring to 0.8 ml of

acid mixture CF_3SO_3H–SbF_5, molar ratio 2:1, at 0°C, and the ^1H and ^{13}C NMR spectra were registered. The degree of conversion of compound **I** into cation **VIII** was ~100%.

1-(1,2,3-trimethyl-1*H*-phenalen-1-yl)ethyl trifluoroacetate (IX). A solution of 30 mg of compound **I** in 0.1 ml CD_2Cl_2 was added to 0.4 ml of CF_3COOH, kept for 5 min at 40°C, and the ^1H and ^{13}C NMR spectra were registered. The degree of conversion of compound **I** into trifluoroacetate **IX** was 95%.

A dispersion 0.105 g (0.448 mmol) of compound **I** in 2.1 ml of CF_3COOH was stirred at room temperature for 3 h (till complete dissolution). CF_3COOH was removed in a vacuum, the residue was dissolved in 2 ml of CCl_4 and the solution was filtered through a bed of chromatographic grade Al_2O_3. The residue after distilling off the solvent in a vacuum (brown oily substance) was according to the ^1H NMR data trifluoroacetate **IX**. Yield 0.10 g (64%). Found *m/z* 348.1327 $[M]^+$. $C_{20}H_{19}F_3O_2$. Calculated *M* 348.1332.

1,2,3-Trimethylphenalenyl cation (V) (cf. [4]). A solution of trifluoroacetate **IX** in CF_3COOH–CD_2Cl_2 was maintained at room temperature for 2 weeks, and the ^1H and ^{13}C NMR spectra were registered. The degree of conversion of trifluoroacetate **IX** into cation **V** was 40%.

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