ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 1, pp. 100–106. © Pleiades Publishing, Inc., 2006.
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Degenerate Rearrangement of Detectable 9,10-Dimethyl-9-vinylphenanthrenium Ion: 1,2-Shift of the Vinyl Group

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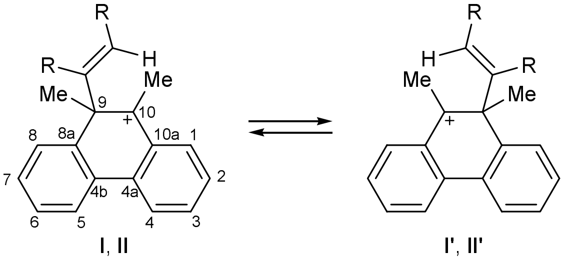
Received September 30, 2004

Abstract—Dynamic NMR study showed that 9,10-dimethyl-9-vinylphenanthrenium ion, generated under the conditions ensuring its "long life," undergoes very fast ($\Delta G^{\neq}$ = 24.4 kJ/mol at –103°C) degenerate 1,2-shift of the vinyl group. According to the DFT quantum-chemical calculations, the process is one-step, and the low energy of formation of the activated complex is determined by effective participation of π electrons of the vinyl group in delocalization of the positive charge; no such delocalization is intrinsic to the initial ion.

DOI: 10.1134/S1070428006010155

We previously reported [1] on degenerate rearrangement of 9,10-dimethyl-9-(*cis*-1-methyl-1-propenyl)phenanthrenium ion (**I**) generated under the conditions ensuring its "long life." It was found that the rearrangement mechanism involves 1,2-shifts of the dimethylvinyl group (Scheme 1). This rearrangement is the first example of direct observation of vinyl group shift in carbocations.

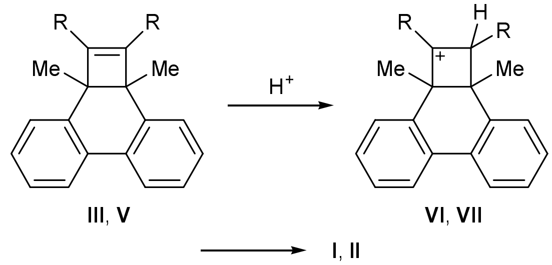
Scheme 1.



I, R = Me; **II**, R = H.

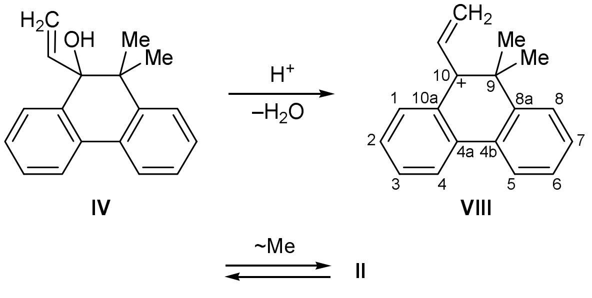
In the present work we made an attempt to "observe" by NMR spectroscopy 1,2-shift of an unsubstituted vinyl group. We anticipated that an appropriate model for this purpose could be 9,10-dimethyl-9-vinylphenanthrenium ion (**II**) generated under analogous conditions. We examined two ways of generating cation **II** in superacids: (1) rearrangement of 2a,10b-dimethyl-2a,10b-dihydrocyclobuta[*l*]phenanthrene (**III**), i.e., a process analogous to generation of cation **I** (Scheme 2), and (2) rearrangement of 9-hydroxy-10,10-dimethyl-9-vinyl-9,10-dihydrophenanthrene (**IV**) (Scheme 3). A rearrangement like that shown in Scheme 3 was reported by us previously for 9-R-9,10-dimethylphenanthrenium ions [2, 3].

Scheme 2.

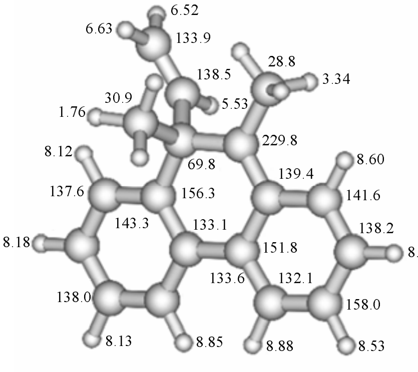


V, **VI**, R = Me; **III**, **VII**, R = H.

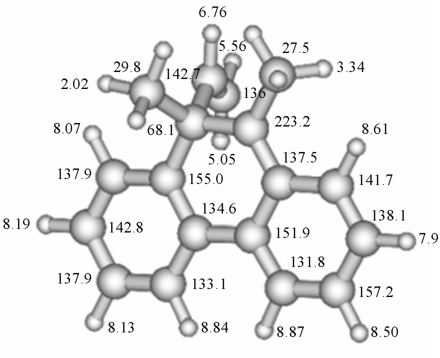
Scheme 3.



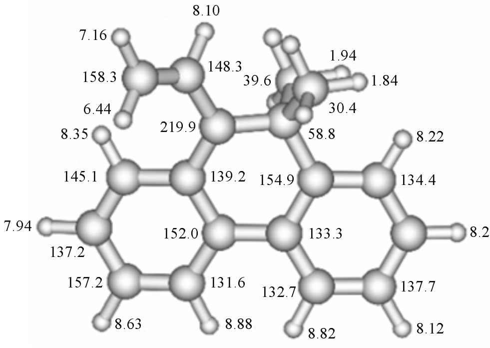
The first way was abandoned, for tetracyclic hydrocarbon **III** seemed to be difficult to obtain; moreover, unlike 1,2,2a,10b-tetramethyl-2a,10b-dihydrocyclobuta[*l*]phenanthrene (**V**) which is protonated to pro-



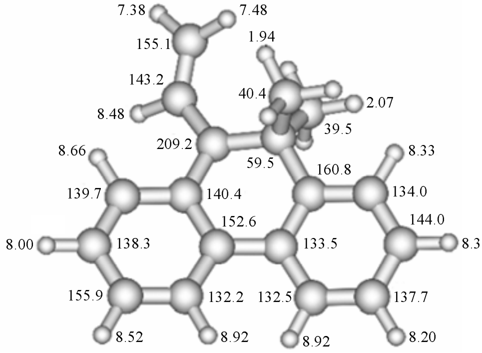
IIA (0.0)



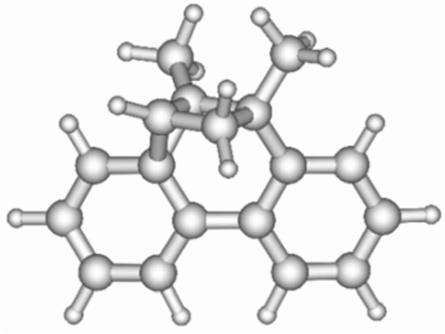
IIB (4.7)



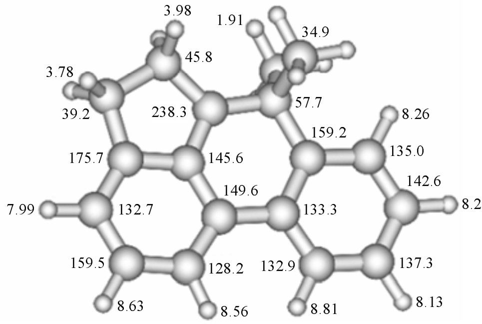
VIIIA (–9.7)



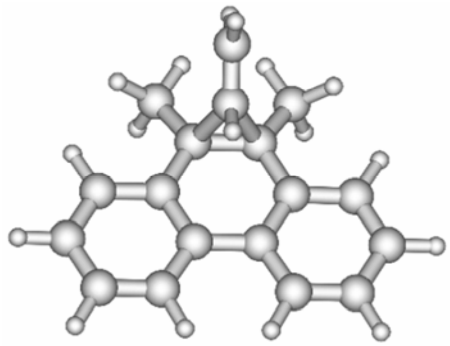
VIIIB (5.2)



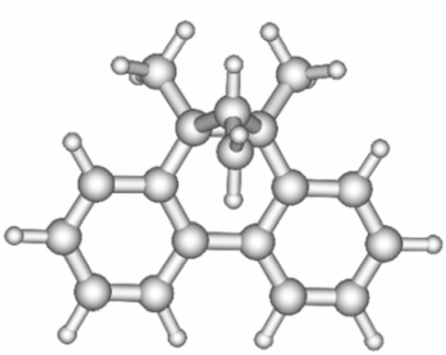
IX (55.0)



XIII (–120.5)



XIIA (22.6)

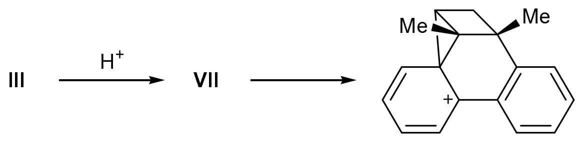


XIIB (37.1)

Calculated structures of the cationic species and transition states for the 1,2-vinyl shift. Given are the calculated ^{1}H and ^{13}C chemical shifts (ppm) and (in parentheses) the relative energies (kJ/mol).

duce tertiary carbocation **VI**, protonation of the double bond in olefin **III** could give rise to much less stable secondary cation **VII**. In this case, the major product obtained from **III** may be a cation whose cleavage would give rise to not ion **II** but some arenium ion resulting from proton addition to an aromatic carbon atom in **III**. Quantum-chemical calculations showed that protonation of **III** at the aromatic rings is more favorable (by 53–105 kJ/mol) than at the double bond. Furthermore, protonation at the double bond gives ion like **IX** rather than **VII**. Cation **VII** does not occupy a minimum on the potential energy surface, while ion **IX** is by 55 kJ/mol less stable than the most stable conformer of ion **II** (structure **IIA**; see figure and Scheme 4).

Scheme 4.



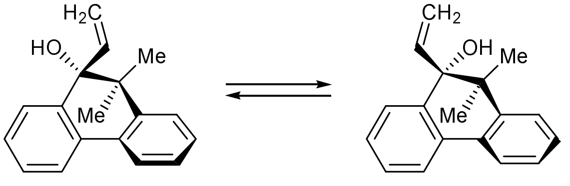
IX

According to the second way for generation of ion **II**, the synthesis of alcohol **IV** from accessible 10,10-dimethyl-10*H*-phenanthren-9-one (**XI**) [4] and its ionization in superacids should not involve difficulties, and isomerization of 9,9-dimethyl-10-vinylphenanthrenium ion (**VIII**) (which is the primary dehydration product of alcohol **IV** protonated at the oxygen atom) to **II** via 1,2-Me shift seems to be feasible (cf. [2]). However, the fraction of β-vinyl-substituted ion **II** in the equilibrium mixture with α-vinyl-substituted isomer **VIII** could be insufficient to attain our goals.

Cation **IIA** turned out to be less stable than the most stable conformer of ion **VIII** (**VIIIA**; see figure) by 9.7 kJ/mol (according to quantum-chemical calculations for the gas phase). Nevertheless, we expected that in a highly polar liquid medium (fluorosulfonic acid), cation **II** in which the positive charge is localized to a greater extent will be stabilized more strongly and that its concentration in the equilibrium mixture with **VIII** will be sufficient to detect it by NMR spectroscopy.

Alcohol **IV** was synthesized by reaction of ketone **XI** with vinylmagnesium bromide. In the ^{1}H and ^{13}C NMR spectra of **IV**, recorded at room temperature, signals from the methyl and vinyl groups were strongly broadened, presumably due to fast conformational transformation shown in Scheme 5; as a result, signals from the pseudoaxial and pseudoequatorial groups in conformers **IV** and **IV'** were averaged (cf. [5].

Scheme 5.



IV **IV'**

As follows from the ^{1}H and ^{13}C NMR data, dissolution of alcohol **IV** in the acid system HSO_3F–SO_2ClF–CD_2Cl_2 at –130°C leads to formation of cation **VIII**. As expected, raising the temperature promotes rearrangement of α-vinyl-substituted cation **VIII** into β-vinyl isomer **II** ($k_{-103°C} = 1.5\times10^{-4}$ s^{-1}, $\Delta G^{\neq}$ = 53.4 kJ/mol). The fraction of **II** in the equilibrium mixture with **VIII** is 13%. The rate of the reverse reaction **II** → **VIII** ($\Delta G^{\neq}$ = 50.7 kJ/mol) is very close to that expected for the isomerization of **I** into 9,9-dimethyl-10-(*cis*-1-methyl-1-propenyl)phenanthrenium ion (**X**) ($\Delta G^{\neq}$ = 50.3 kJ/mol) [1]. This means that "expelling" effects of unsubstituted vinyl and dimethylvinyl groups in 9-R-9,10-dimethylphenanthrenium ions are almost similar. It should be noted that quantum-chemical calculation of the energy barrier (i.e., the energy difference between the most stable conformations of the transition and initial states) to 1,2-shift of the CH_3 group in **II** gives a value of 61.4 kJ/mol, and for analogous process in cation **I**, 57.6 kJ/mol.

The ^{1}H NMR spectrum of cation **II** at –103°C indicates that it undergoes fast degenerate rearrangement which leads to averaging of the methyl proton signals and averaging of the aromatic proton signals in pairs, δ, ppm: 2.63 s (6H, 9-CH_3, 10-CH_3), 5.69 d.d (1H, C**H**=CH_2, *J* = 10, 17 Hz), 6.08 d (1H, *cis*-CH=C**H**$_2$, *J* = 10 Hz), 6.18 d (1H, *trans*-CH=C**H**$_2$, *J* = 17 Hz), 7.85–7.95 (2H, 2-H, 7-H),* 8.23 t (2H, 3-H, 6-H, *J* = 7 Hz), 8.31 d (2H, 1-H, 8-H, *J* = 8 Hz), 8.65–8.8 (2H, 4-H, 5-H).* In the ^{13}C NMR spectrum at –103°C we observed signals at δ_C 26.3 (9-CH_3, 10-CH_3), 122.0 (CH_2=CH), and 132.3 ppm (**C**H=CH_2), as well as broadened signals at δ_C 133.5 (C^{1}/C^{8} or C^{4}/C^{5}, $W_{1/2}$ = 17 Hz)** and 140.2 ppm (C^{4a}/C^{4b}, $W_{1/2}$ = 40 Hz). The

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* The signal is obscured by those of the major component (**VIII**), as follows from overall signal intensity in the given region.

** Hereinafter, $W_{1/2}$ stands for the signal half-width (width at the half-height).

other carbon signals were either strongly broadened or overlapped by those belonging to the major component, cation **VIII**. The signals were assigned by analogy with the NMR spectra of **I** [1].

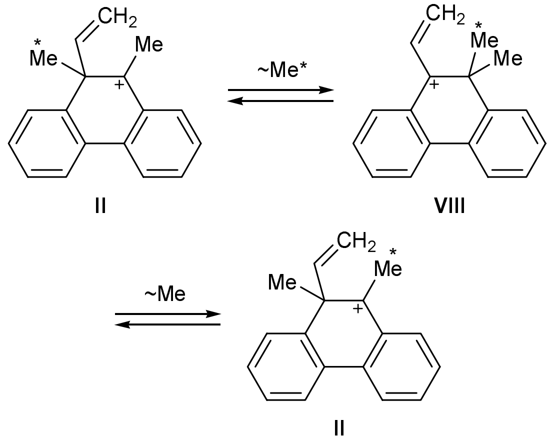
According to the calculations, the vinyl group in both conformers **IIA** and **IIB** is arranged with respect to the vacant *p* orbital of the cationic carbon atom in such a way that π–p interaction is possible. However, the contribution of this interaction is small (if exists). In keeping with the data of [6], the energy of such interaction even in unsubstituted allylmethyl cation does not exceed 12.5 kJ/mol. Therefore, the barrier to rotation of the vinyl group in **II** (24.5 kJ/mol) is likely to originate mainly from steric factor rather than from π–p interaction.

The rate of degenerate rearrangement of ion **II** was estimated by the dynamic NMR technique using the program reported in [7]: $k_{-103°C} = 1.1\times10^5\ s^{-1}$, $\Delta G^{\neq}$ = 24.4 kJ/mol. The chemical shifts of methyl protons in the “frozen” structure (the corresponding signals could not be observed even at low temperature because of fast rate of the rearrangement) were determined by quantum-chemical calculations: δ 1.76 (9-CH_3) and 3.34 ppm (10-CH_3). These values approach those found experimentally for structurally related 9-R-9,10-dimethylphenanthrenium ions (R = H, Me, Et) [3, 8, 9].

Obviously, the observed degenerate rearrangement of cation **II** involves 1,2-shift of the vinyl group. Alternative mechanisms seem to be improbable. They were considered in detail by us previously [1] as applied to 1,2-shift of the dimethylvinyl group in **I**. Reversible 1,2-shift of the methyl group in **II** according to Scheme 6, which could simulate 1,2-migration of the vinyl group thus leading to the observed averaging of the methyl proton signals, does not occur: the rate of the reaction **II** → **VIII** and of the reverse process is much lower than the rate of degenerate rearrangement of ion **II**; moreover, 1,2-shift of the methyl group should not result in averaging of the aromatic proton signals.

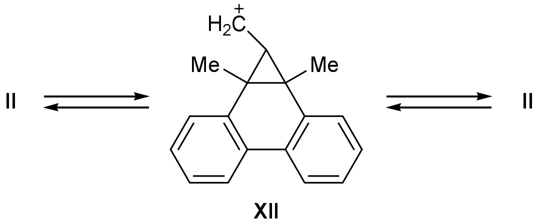
The fact that the rate of 1,2-vinyl shift is much higher than the rate of migration of other hydrocarbon groups (except for dimethylvinyl group) [1, 10] suggests that π electrons of the double bond effectively participate in delocalization of positive charge in the activated complex and that the 1,2-vinyl shift is not purely sigmatropic (cf. [11, 12]). In the latter case, the energy barrier should be much higher than that observed experimentally. According to *ab initio* calculations [13], bisected cyclopropylcarbinyl cation, which simulates the transition state for 1,2-vinyl shift with participation of double bond π electrons, is more stable by 149.3 kJ/mol than “orthogonal” cyclopropylcarbinyl cation, which simulates the transition state for purely sigmatropic shift. The absence of averaging of signals from the β-vinyl protons in the ^1H NMR spectra of **II** also argues against purely sigmatropic shift.

Scheme 6.



A question arises as to whether 1,2-vinyl shift is a single-step process or it involves cyclopropylcarbinyl-like intermediate, cation **XII** (Scheme 7)? Downfield shift of the =CH_2 proton signals in going from alcohol **IV** to ion **II** could be considered to be an argument in favor of formation of relatively stable intermediate **XII**. However, analogous results were obtained by quantum-chemical calculations of the chemical shifts of the corresponding protons in **II** (see table).

Scheme 7.



An evidence against the two-step mechanism of the 1,2-vinyl shift (Scheme 7) may be the absence of averaging of the β-vinyl proton signals in the ^1H NMR spectrum of cation **II**; this averaging could result from rotation about the C–C^+ bond in **XII**. However, the barrier to such rotation in cyclopropylcarbinyl type cations is known to be very high (for example, it exceeds 146 kJ/mol for unsubstituted cyclopropylcarbinyl cation [13]). Therefore, the absence of averaging of the β-vinyl proton signals cannot be regarded as an argument against Scheme 7. Quantum-

Experimental and calculated ^1H and ^{13}C chemical shifts of the β-vinyl fragment (=CH_2) in the NMR spectra of alcohol **IV** and ion **II**, δ or δ_C, ppm

Atom	Experiment		Calculation	
	II	**IV**	**IIA**	**IV**[a]
β-C	122.0	113.3	133.9	119.2
cis-β-H	6.08	5.13	6.62	5.44
trans-β-H	6.18	5.47	6.63	5.95

[a] Half-sum of values corresponding to the most stable conformers with pseudoaxial and pseudoequatorial vinyl group.

chemical calculations of the energy profile for 1,2-vinyl shift in ion **II** show that the process is one-step, and the calculated energy barrier (22.6 kJ/mol) approaches the experimental value (24.4 kJ/mol). Likewise, a one-step mechanism is predicted by calculations for 1,2-shift of the *cis*-dimethylvinyl group in cation **I** [1]. In keeping with these results, no compounds having a cyclopropane fragment were detected among the products obtained by neutralization of acid solution of **I** fluorosulfonate [14]. The calculated energy difference between the activated complexes corresponding to 1,2-vinyl shift in conformers **IIA** and **IIB** is 14.4 kJ/mol. An analogous value is typical of cation **I** (15.2 kJ/mol) [1]. Obviously, the reason is not steric factor, for the corresponding energy difference for 1,2-shift of the vinyl group in model 1-vinylbenzenium ion (where the contribution of steric factor is negligible) reaches 26.6 kJ/mol. Presumably, the activated complex in which the β-vinyl carbon atom hangs over the aromatic rings possesses a greater energy since the *p* orbital of that atom lies in the plane parallel to the aromatic rings, i.e., their mutual arrangement is unfavorable for *p*–π interaction.

Comparison of the rates of 1,2-migrations of the vinyl group in **II** and *cis*-dimethylvinyl group in **I** ($k_{-120°C} = 1\times10^5\ s^{-1}$, $\Delta G^{\neq} = 22.0$ kJ/mol) [1] shows that replacement of hydrogen atoms in the vinyl group by electron-donor methyl groups favors the migration process; however, the observed effect is not strong. A probable reason is greater strain in the transition state for 1,2-shift of the dimethylvinyl group due to unfavorable steric interaction between one of the methyl groups and phenanthrene skeleton. The experimental data are consistent with the results of quantum-chemical calculations, according to which the activation barriers to 1,2-shift of the vinyl group in **II** and *cis*-dimethylvinyl group in **I** are 18.8 and 22.6 kJ/mol, respectively.

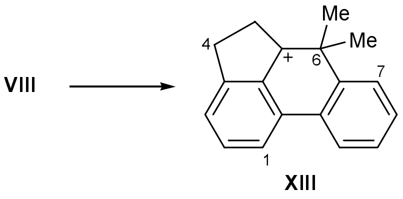
It was interesting to compare the Gibbs energy of activation for degenerate 1,2-shift of the vinyl group in cation **II** with the value calculated from correlation (1) [15]; the latter was deduced from the kinetic data for 1,2-shifts of various migrating groups (Y = Me, Et, XC_6H_4, Cl, Br) in arenium ions.

$$\Delta G^{\neq}(-110°C) = 2.6\pm0.313E_d - 0.00133PA(\delta_{C^+} - 130). \quad (1)$$

Here, E_d is the energy of dissociation of the Y–CH_3 bond (kcal/mol), *PA* is the proton affinity of YCH_3 (kcal/mol), and δ_{C^+} is the chemical shift of the cationic carbon atom (to which the migrating group is transferred). For propene, $E_d = 95.1$ [16], $PA = 179.6$ kcal× mol^{-1} [17]. The δ_{C^+} value (which is unavailable experimentally) was determined by quantum-chemical calculations. For the most populated conformation **IIA** of ion **II**, it is equal to 229.8 ppm, i.e., it almost coincides with the value found experimentally for structurally related 9,10-dimethyl-9-phenylphenanthrenium ion (229.5 ppm) [18]. Substituting these values into Eq. (1) gives $\Delta G^{\neq} = 8.53$ kcal/mol which differs from the value obtained by the dynamic NMR technique ($\Delta G^{\neq}$ = 24.4 kJ/mol or 5.83 kcal/mol); this inconsistence is likely to indicate a limited scope of correlation (1).

Apart from the rearrangement to give ion **II**, ion **VIII** is capable (like its dimethyl-substituted analog [14]) to undergo cyclization to afford 6,6-dimethyl-4,5-dihydro-6*H*-cyclopenta[1,2,3-*de*]phenanthren-5a-yl cation (**XIII**) (Scheme 8; cf. [14]). When a solution containing ions **VIII** and **II** ($HSO_3F–SO_2ClF–CD_2Cl_2$) warmed up to –30°C, signals belonging to these cations completely disappeared from the ^1H and ^{13}C NMR spectra, and the latter contained only signals from cation **XIII**.

Scheme 8.



The formation of the only rearrangement product is important from the practical viewpoint, for the rearrangement provides a selective route to a fairly complex cyclic system.

EXPERIMENTAL

The NMR spectra of cationic species were recorded on a Bruker AM-400 spectrometer using CD_2Cl_2 as internal reference (δ 5.33, δ_C 53.3 ppm). The temperature in the probe of the spectrometer was calibrated against *n*-pentane (mp –130°C) and methanol (above –90°C) using linear interpolation. The geometric parameters and NMR chemical shifts of carbocations were calculated in terms of the density functional theory (DFT) in the PBE approximation [20] using *Priroda* software [21] {triple-zeta basis set, (11*s*6*p*2*d*)/[6*s*3*p*2*d*] for carbon and oxygen atoms and (5*s*1*p*)/[3*s*1*p*] for hydrogen atoms}. Exchange NMR spectra were calculated using MEX program [7].

Ketone **XI** was synthesized by the procedure reported in [4] using a solution of vinylmagnesium bromide in tetrahydrofuran (Aldrich). Fluorosulfonic acid was distilled twice (bp 158–161°C), SO_2ClF [19] was dried by passing its vapor through concentrated sulfuric acid, and CD_2Cl_2 was dried over 4-Å molecular sieves.

9-Hydroxy-10,10-dimethyl-9-vinyl-9,10-dihydrophenanthrene (IV). A solution of 2.22 g (10 mmol) of ketone **XI** in 5 ml of THF was added over a period of 2 h to a solution of 15 ml (15 mmol) of vinylmagnesium bromide in THF while stirring under argon at room temperature. The mixture was then heated for 2 h at 50°C and cooled to 0°C, and 10 ml of a saturated aqueous solution of NH_4Cl was added. Alcohol **IV** was extracted into hexane (5 × 10 ml), and the extract was washed with a saturated aqueous solution of sodium chloride, dried over Na_2SO_4, and evaporated under reduced pressure. According to the NMR data, the residue, 2.62 g (a light yellow oily substance), was alcohol **IV** with an impurity of hexane which cannot be removed even by prolonged evacuation at 50°C; nevertheless, it can be used for generation of ion **VIII**. Vacuum distillation at a bath temperature of 150°C (0.5 mm) gave 1.23 g (50%) of a colorless oily substance. IR spectrum (CCl_4), ν, cm^{-1}: 3617 m, 3070 m, 2976 s, 2935 m, 2873 w, 1948 w, 1914 w, 1839 w, 1806 w, 1637 w, 1601 w, 1483 s, 1448 m, 1408 s, 1384 m, 1362 m, 1315 m, 1300 m, 1277 m, 1202 m, 1162 m, 1108 m, 1085 m, 1044 m, 993 s, 922 s, 894 m, 803 m. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.28 s (3H, 10-CH_3, $W_{1/2}$ = 6 Hz),*** 1.51 s (3H, 10-CH_3, $W_{1/2}$ = 5 Hz), 2.20 s (1H, OH), 5.13 d (1H, *cis*-CH=C**H**$_2$, *J* = 11 Hz, $W_{1/2}$ = 12 Hz), 5.47 d (1H, *trans*-CH=C**H**$_2$, *J* = 17 Hz, $W_{1/2}$ = 8 Hz), 6.12 d.d (1H, C**H**=CH_2, *J* = 11, 17 Hz, $W_{1/2}$ = 5 Hz), 7.36–7.56 m (5H, H_{arom}), 7.70–7.78 m (1H, H_{arom}), 7.82–7.94 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.1 q ($W_{1/2}$ = 40 Hz), 23.6 q ($W_{1/2}$ = 16 Hz), 42.0 s, 78.7 s, 113.3 t ($W_{1/2}$ = 22 Hz), 123.4 d, 123.7 d, 124.6 d ($W_{1/2}$ = 11 Hz), 124.9 d, 126.7 d, 127.6 d, 128.1 d, 128.2 d, 132.3 s, 132.5 s, 139.7 d ($W_{1/2}$ = 5 Hz), 140.2 s ($W_{1/2}$ = 5 Hz), 143.6 s. Found: *m*/*z* 250.1470 $[M]^+$. $C_{18}H_{18}O$. Calculated: *M* 250.1358.

9,9-Dimethyl-10-vinylphenanthrenium fluorosulfonate (VIII). An NMR ampule was charged with 0.2 ml (3.45 mmol) of HSO_3F and cooled to –90°C, 0.2 ml of SO_2ClF was added, and the mixture was stirred. An additional 0.1 ml of SO_2ClF was layered at the top, the ampule was transferred to a Dewar flask charged with frozen pentane (–130°C), and a solution of 65 mg (0.26 mmol) of alcohol **IV** in 0.1 ml of CD_2Cl_2 was added. After 5 min, the mixture was stirred with a glass rod cooled with liquid nitrogen to obtain a violet solution. ^1H NMR spectrum (–103°C), δ, ppm: 1.93 s (6H, 9-CH_3), 6.22 d (1H, *trans*-CH=C**H**$_2$, *J* = 16 Hz), 6.94 d (1H, *cis*-CH=C**H**$_2$, *J* = 11 Hz), 7.77 t (1H, H_{arom}, *J* = 8 Hz), 7.8–7.95 m (3H, H_{arom}, C**H**=CH_2), 8.05 d (1H, H_{arom}, *J* = 8 Hz) 8.49 d (1H, H_{arom}, *J* = 8 Hz), 8.62 d (1H, H_{arom}, *J* = 8 Hz), 8.69 t (1H, H_{arom}, *J* = 8 Hz), 8.76 d (1H, H_{arom}, *J* = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.6 q (9-CH_3, *J* = 133 Hz), 50.0 s (C^9), 125.5 d.d (C_{arom}, *J* = 166, 6 Hz), 126.3 d.d (C_{arom}, *J* = 161, 7 Hz), 126.6 s (C^{10a} or C^{4b}), 127.3 d.d (C_{arom}, *J* = 160, 8 Hz), 129.0 d.d (C_{arom}, *J* = 165, 7 Hz), 130.5 d.d (C_{arom}, *J* = 170, 7 Hz), 132.6 s (C^{4b} or C^{10a}), 134.2 d.d (C_{arom}, *J* = 164, 8 Hz), 137.4 d (**C**H=CH_2, *J* = 165 Hz), 141.9 d.d (C_{arom}, *J* = 170, 6 Hz), 146.4 s (C^{4a} or C^{8a}), 148.4 s (C^{8a} or C^{4a}), 148.6 t (CH=**C**H_2, *J* = 166 Hz), 152.8 d.d (C^3, *J* = 165, 8 Hz), 222.8 s (C^{10}).

6,6-Dimethyl-4,5-dihydro-6*H*-cyclopenta[1,2,3-*de*]phenanthren-5a-ium fluorosulfonate (XIII). A solution containing cations **VIII** and **II** was allowed to warm up to –30°C in the probe of NMR spectrometer, and the solution turned red. ^1H NMR spectrum (–30°C), δ, ppm: 1.96 s (6H, 6-CH_3), 3.77 s (2H, 4-H or 5-H), 4.00 s (2H, 5-H or 4-H), 7.76 t (1H, 9-H, *J* = 7.5 Hz), 7.88 t (1H, 8-H, *J* = 7.6 Hz), 7.98 d (1H, 3-H, *J* = 7.4 Hz), 8.06 d (1H, 7-H, *J* = 8.1 Hz), 8.46 d (1H, 1-H, *J* = 7.8 Hz), 8.56 d (1H, 10-H, *J* = 8.0 Hz), 8.69 t (1H, 2-H, *J* = 7.5 Hz). ^{13}C NMR spectrum (–30°C), δ_C, ppm: 29.7 q.q (6-CH_3, *J* = 133.6, 4.6 Hz), 33.7 t (C^4, *J* = 136.1), 41.1 t.t (C^5, *J* = 132.6, 2.7 Hz), 49.6 s (C^6), 123.0 d.d.d (*J* = 165.8, 6.6, 1.9 Hz), 126.9 d.d (*J* = 160.4, 7.6 Hz), 127.0 s (C^{10a}), 127.2 d.d (*J* = 170.4, 7.2 Hz), 128.1 d.d (*J* = 160.4,

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*** Hereinafter, $W_{1/2}$ is the half-width (width at the half-height) of signals (multiplet components) for which it is not lesser than 5 Hz.

7.6 Hz), 129.3 d.d (J = 164.8, 7.8 Hz), 133.9 d.d (C^8, J = 164, 8.8 Hz), 140.2 s (C^{10c}), 145.6 s (C^{10b}), 149.7 s (C^{6a}), 155.8 d (C^2, J = 161.8 Hz), 172.3 s (C^{3a}), 238.9 s (C^{5a}); the signals were assigned by analogy with the spectra of *trans*- and *cis*-4,5,6,6-tetramethyl-4,5-dihydro-6*H*-cyclopenta[1,2,3-*de*]phenanthren-5a-yl cations reported in [14].

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 02-03-32881).

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