

Degenerate Rearrangement of 9-Isopropenyl-9,10-dimethylphenanthren-9-yl and 9,10-Dimethyl-9-(*trans*-1-methylprop-1-en-1-yl)phenanthren-9-yl Cations

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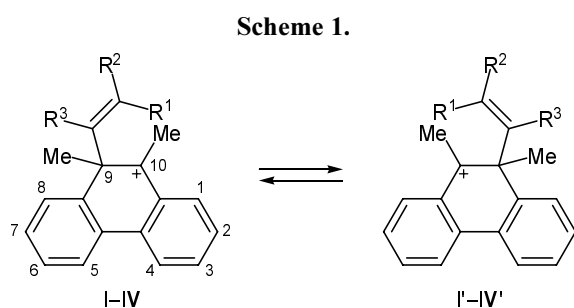
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Abstract—¹H NMR study has shown that long-lived 9-R-9,10-dimethylphenanthren-9-yl cations (R = isopropenyl, *trans*-1-methylprop-1-en-1-yl) generated in the system HSO₃F–SO₂ClF–CD₂Cl₂ at –130°C undergo degenerate rearrangement via 1,2-vinyl shifts ($\Delta G^\ddagger = 37$ and 39 kJ/mol, respectively, at –88°C). Analysis of the geometric parameters of the initial structures and transition states calculated by the DFT method indicates that unfavorable steric factors are responsible for the sharp deceleration of 1,2-shifts of the isopropenyl and *trans*-1-methylprop-1-en-1-yl groups as compared to vinyl and *cis*-1-methylprop-1-en-1-yl groups, respectively.

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We briefly reported in [1] on unexpectedly strong inhibition of vinyl group migrations in going from 9,10-dimethyl-9-vinylphenanthren-9-yl cation (**I**) [2] to 9-isopropenyl-9,10-dimethylphenanthren-9-ylum (**II**) and from 9,10-dimethyl-9-(*cis*-1-methylprop-1-en-1-yl)phenanthren-9-ylum (**III**) [3, 4] to 9,10-dimethyl-9-(*trans*-1-methylprop-1-en-1-yl)phenanthren-9-ylum (**IV**) (Scheme 1). The goal of the present study was to elucidate reasons for the observed inhibition.

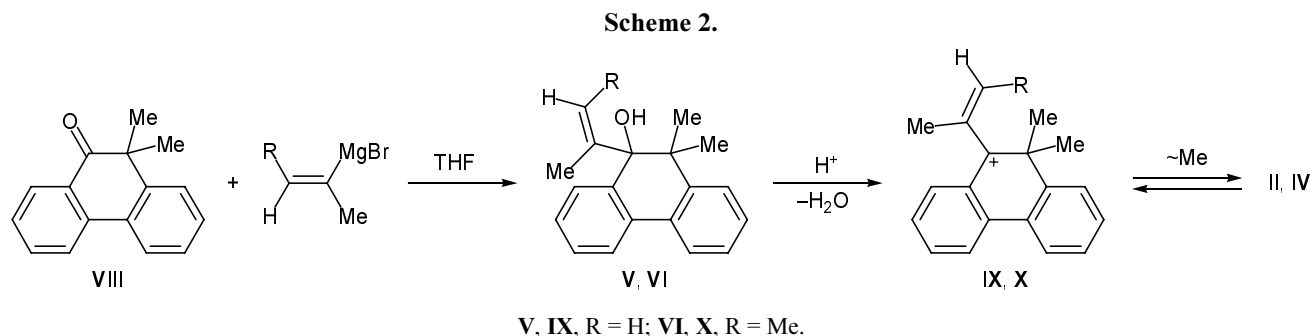


I, R¹ = R² = R³ = H; **II**, R¹ = R² = H, R³ = Me; **III**, R¹ = H, R² = R³ = Me; **IV**, R¹ = R³ = Me, R² = H.

As starting compounds for the generation of long-lived cations **II** and **IV** we selected 9-isopropenyl-10,10-dimethyl-9,10-dihydrophenanthren-9-ol (**V**) and 10,10-dimethyl-9-(*trans*-1-methylprop-1-en-1-yl)-

9,10-dihydrophenanthren-9-ol (**VI**). These alcohols are derivatives of 10,10-dimethyl-9-vinyl-9,10-dihydrophenanthren-9-ol (**VII**) which was successfully used by us previously to generate cation **I**, an analog of ions **II** and **IV** [2]. Compounds **V** and **VI** were synthesized by reaction of 10,10-dimethylphenanthren-9(10*H*)-one (**VIII**) [5] with organomagnesium compounds prepared from the corresponding vinyl bromides (Scheme 2). In the synthesis of alcohol **VI** we used a mixture of bromides obtained by dehydrobromination of 2,3-dibromobutane. The coupling constant $^5J_{\text{HH}} = 1.5$ Hz for protons of the CH₃ groups in the propenyl fragment of the alcohol isolated from the product mixture indicates *trans* arrangement of these groups [6].

The ¹H and ¹³C NMR spectra of solutions of alcohols **V** and **VI** in the acid system HSO₃F–SO₂ClF–CD₂Cl₂ at –130°C indicate formation of cations **II** and **IV**, respectively (Scheme 2). Figure 1 shows the ¹H NMR spectra of cation **II**. Its formation was deduced by comparing the spectrum recorded at –107°C with those of related 9-R-9,10-dimethylphenanthren-9-yl cations [2–4, 7]. The ¹³C NMR spectrum contained a set of signals typical of such cations [8]. In the ¹H NMR spectrum of a solution of alcohol **VI** at –109°C we observed two groups of signals with dif-



ferent intensities, δ , ppm: (1) 0.57 d (3H, $J = 7$ Hz), 1.73 s (3H), 2.51 s (3H), 3.41 s (3H), 5.71 q (1H, $J = 7$ Hz) and (2) 1.50 d (3H, $J = 7$ Hz), 1.89 s (3H), 2.03 s (3H), 2.33 s (3H), 6.26 q (1H, $J = 7$ Hz). In addition, two unresolved multiplet signals with equal intensities were present at δ 7.7–8.2 and 8.4–8.9 ppm; these signals belong to protons in the aromatic rings. By analogy with the ionization of alcohol **VII** having an unsubstituted vinyl group on C⁹ [2] and taking into account the presence in the ¹H NMR spectrum of a singlet at δ 3.41 ppm, which is typical of the ⁺C¹⁰–CH₃ fragment in 9-substituted 9,10-dimethylphenanthren-

ylium ions (see [4] and references therein), the first set of signals should be assigned to target cation **IV**, and the second, to 9,9-dimethyl-10-(*trans*-1-methylprop-1-en-1-yl)phenanthren-9-ylum (**X**) formed initially from hydroxy compound **VI** (Scheme 2). Obviously, cation **X** exists in equilibrium with ion **IV**; according to the CH₃ signal intensities, the ratio of cations **IV** and **X** is 3:1. Like cation **II**, the ¹³C NMR spectrum of ion **IV** contains a set of signals typical of 9-substituted 9,10-dimethylphenanthren-9-yl cations [8].

The results of quantum-chemical calculations showed that each cation **II** and **IV** can exist in two

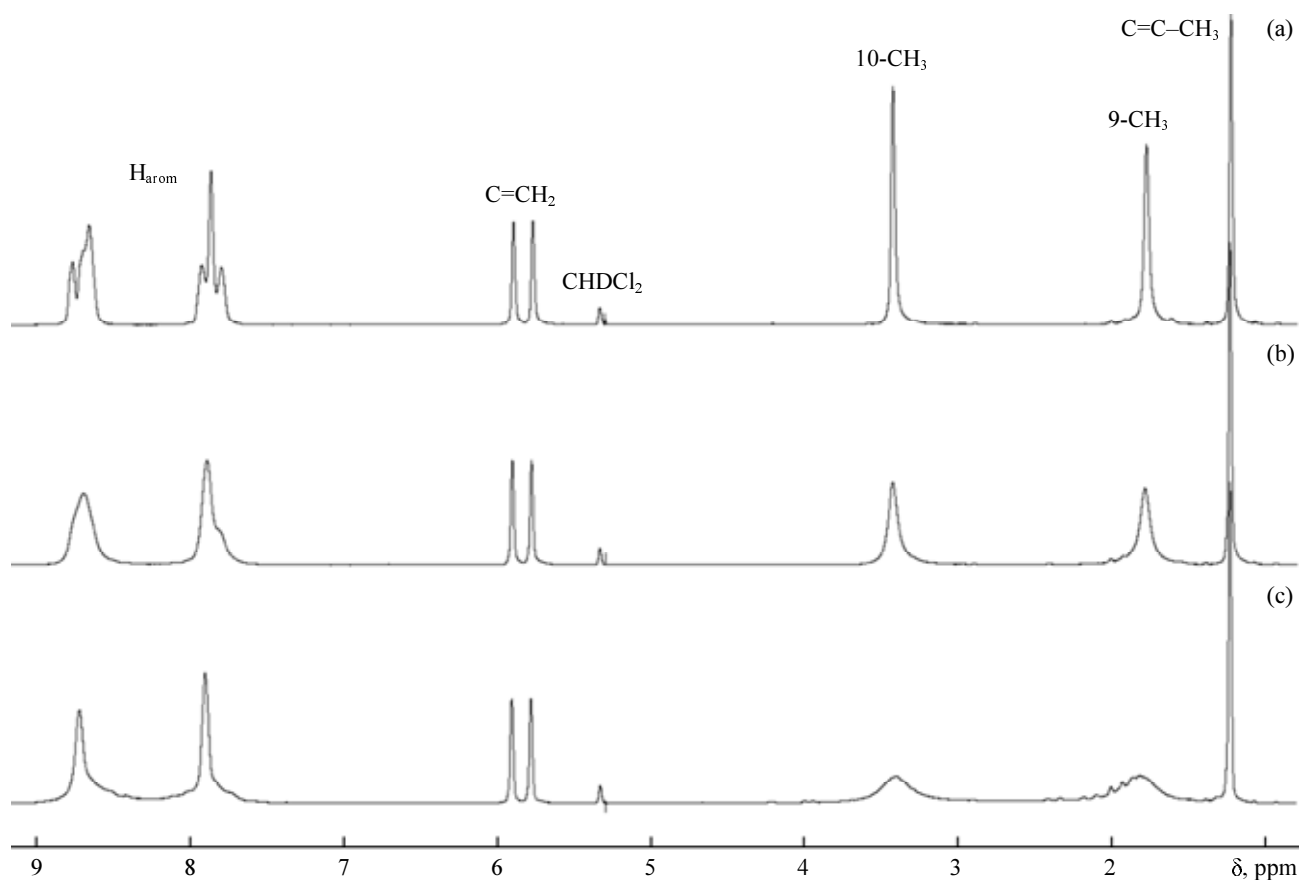
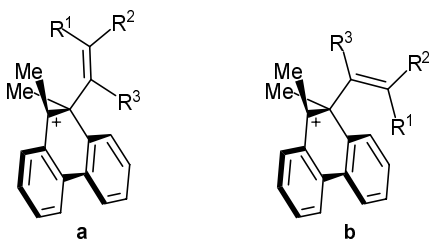


Fig. 1. ¹H NMR spectra of 9-isopropenyl-9,10-dimethylphenanthren-9-ylum (**II**) at (a) –107°C, (b) –97°C, and (c) –86°C.

stable conformations: **a** (where the vinyl double bond axis is almost parallel to the aromatic ring plane) and **b** (where the vinyl group hangs over the aromatic rings). Among these, conformer **IIa** is more stable for cation **II**, and conformer **IVb** is more stable for ion **IV** (see below, Table 2). In keeping with the above stated, in both cases the calculated chemical shifts for the more stable conformations are much more similar to the experimental values (Table 1).



Comparison of the ^1H NMR spectrum of cation **IV** with the spectrum of cation **III** reported previously [3, 4] revealed considerable differences in the chemical shifts of protons in the dimethylvinyl groups. In the spectrum of **IV**, signals from the terminal vinyl protons (δ 5.71 ppm) and CH_3 group (δ 0.57 ppm) are displaced strongly upfield, while the signal of the other methyl group at the double bond is displaced downfield (by 1.44 ppm). Presumably, the reason is anisotropy of magnetic shielding by the aromatic rings of the dimethylvinyl groups in conformers **IIIa** and **IVb**.

Ions **II** and **IV**, as well as **I** and **III** [2, 4], give rise to dynamic equilibria: as the temperature rises, the ^1H NMR spectra show reversible changes suggesting that these ions undergo degenerate rearrangements. However, the spectra of cations **I** and **III** were typical of fast exchange (averaged signals from the 9- and 10- CH_3 protons were observed) even at the lowest experimentally attainable temperature (down to -130°C), while the 9- and 10- CH_3 signals in the spectra of cations **II** and **IV** appeared separately (slow exchange; Fig. 1). We failed to observe their fast exchange, for ions **II** and **IV** are unstable above -80°C .

Presumably, the rearrangement mechanism involves 1,2-migrations of the vinyl groups. Alternative paths seem to be improbable (they were analyzed in detail previously [4] as applied to 1,2-shifts of the *cis*-dimethylvinyl group in cation **III** and were ruled out with a sufficient reliability). There are no reasons to believe that the rearrangement mechanism could change in going from ion **III** to **II** and **IV**.

By the dynamic NMR technique in the temperature range from -112 to -81°C (10 points) we determined

Table 1. Experimental and calculated proton chemical shifts δ , ppm, in the ^1H NMR spectra of cations **II** and **IV**

Cation	R ¹	R ²	R ³	9-CH ₃	10-CH ₃
II (exptl.)	5.89	5.77	1.22	1.77	3.42
IIa	6.24	6.26	1.38	1.75	3.41
IIb	4.58	5.15	2.68	1.90	3.25
IV (exptl.)	0.57	5.71	2.51	1.73	3.41
IVa	2.50	6.85	1.24	1.92	3.50
IVb	0.76	6.13	2.63	1.75	3.30

the following kinetic parameters for the degenerate rearrangement of ion **II**: $E_a = 40.9 \pm 2.0$ kJ/mol, $\log A = 13.8 \pm 0.6$, $\Delta G^\ddagger = 37.1\text{--}36.4$ kJ/mol, $\Delta H^\ddagger = 39.4 \pm 2.0$ kJ/mol, $\Delta S^\ddagger = 15 \pm 11$ J mol⁻¹ K⁻¹. Cation **IV** is less stable than **II**, and the rate of its degenerate rearrangement is lower; we succeeded in determining the rate of degenerate rearrangement of ion **IV** only at -88°C : $k = 40$ s⁻¹, $\Delta G^\ddagger = 39$ kJ/mol.

According to the calculations (Table 2), the rearrangement of ion **II**, as well as of **I** and **III**, involves conformer **a** as initial structure and type **A** transition state (TS): These species have lower energies than conformer **b** and TS like **B**. The situation with cation **IV** is different: TS like **A** also has a lower energy, but conformer **IVb** is more stable. Nevertheless, the rearrangement occurs through transition state **IVB** rather than along the three-step scheme **IVb** \leftrightarrow **IVa** \leftrightarrow **IVa'** \leftrightarrow **IVb'** (Scheme 3), for the barrier to the transformation **IVb** \leftrightarrow **IVb'** is lower than the barrier to the conformational transition **IVb** \leftrightarrow **IVa** (Table 2).

Comparison of the obtained experimental kinetic parameters with those reported previously for the degenerate rearrangements of cations **I** [2] and **III** [3, 4] (Table 2) shows that the rate of the process sharply drops down (by 4 to 5 orders of magnitude) in going to ions **II** and **IV**. Furthermore, no acceleration of degenerate rearrangement was observed in going from **II** to **IV** (Table 2), though it might be expected taking into account reduced transition state energy due to replacement of the β -hydrogen atom in the migrating group by electron-donor methyl group. Replacement of the α -hydrogen atom in the vinyl fragment by CH_3 (in going from ion **I** to **II**) and change of the configuration (cf. structures **III** and **IV**) are unlikely to induce an appreciable reduction of the nucleophilicity of the migrating groups, i.e., their ability to form cyclopropylcarbinyl transition states in reactions with a cationic center (Scheme 3). Also, reduction of the rate of degenerate rearrangement of ion **II** compared

Table 2. Calculated relative energies (kJ/mol) of different conformations of the initial ions and transition states and experimental kinetic parameters of degenerate rearrangements of cations **I–IV**

Cation	Conformation ^a		Transition state ^a			Barrier to rearrangement		$k, ^b \text{ s}^{-1} (-103^\circ\text{C})$
	a	b	A	B	^c	calculated ^a	experimental ^d	
I	0.0	4.7	22.6	37.0	24.5	22.6	24 (-103)	1×10^5
II	0.0	11.0	38.3	51.5	32.0	38.3	39	10
III	0.0	7.8	18.8	33.1	25.2	18.8	22 (-120)	6×10^5
IV	10.4	0.0	35.1	36.3	43.1	36.3	39 (-88)	4

^a In each line, the energy of the most stable conformation was assumed to be equal to zero.

^b Calculated by the Eyring equation.

^c Energy of the transition state for the transformation $\mathbf{a} \rightleftharpoons \mathbf{b}$.

^d ΔG^\ddagger for the degenerate rearrangement of cations **I**, **III**, and **IV**; the temperature ($^\circ\text{C}$) is given in parentheses; ΔH^\ddagger for the degenerate rearrangement of cation **II**.

to **I** cannot result from inhibitory electronic effect (like that presumed by us previously [2] for vinyl migrations involving type **B** transition states), for the degenerate rearrangement of **II** occurs through TS like **A** (Fig. 2). The observed deceleration of the rearrangements is likely to be determined by steric factor.

For example, a probable reason for the observed inhibition of the degenerate rearrangement of cation **II** relative to **I** is unfavorable spatial interaction between the methyl group of the migrating vinyl fragment with the molecular skeleton in the transition state. This assumption is confirmed by the results of calculations (Table 3): the difference $\nu_{\text{CH}} - d_1$ characterizing the above interaction in ion **II** is larger. Moreover, from the data in Table 3 it follows that this interaction induces some rotation of the migrating fragment about the $\text{C}^9\text{--C}^{10}$ bond; as a result, the angle α_1 and the difference $\nu_{\text{CH}} - d_2$ increase considerably. The latter parameter also increases for the initial states, but to a smaller extent. It should be noted that the carbon–carbon bond length (l) between the migrating group and the cyclic skeleton and the angle characterizing deviation of the skeleton atoms from the plane ($180^\circ - \alpha_2$) in the transition state for the degenerate rearrangement of ion **II** are larger than the corresponding parameters for ion **I**. Obviously, steric factors are

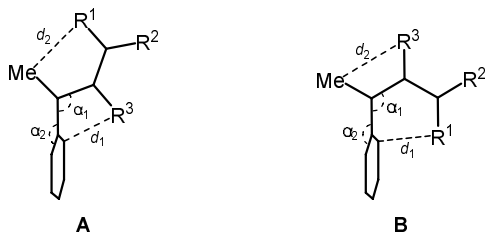


Fig. 2. Projections of the transition state structures along the $\text{C}^9\text{--C}^{10}$ axis.

also responsible for deceleration of the degenerate rearrangement in going from ion **III** to **IV**. In this case, their effects are similar for both initial and transition states (Table 3). Probably, inhibitory electronic effect [2] (see above) also makes some contribution to the rearrangement of cation **IV**, where the initial state has conformation like **b**.

Finally, when solutions of cations **IV** and **X** (with fluorosulfonate as counterion), prepared at -130°C , were kept for 1.5–2 h at -100°C , signals of these species disappeared from the ^1H NMR spectrum, and the spectrum contained signals corresponding to a mixture of *trans*- and *cis*-4,5,6,6-tetramethyl-4,5,5a,6-tetrahydrocyclopenta[*j,k*]phenanthren-5a-yl cations (**XI**). The formation of isomeric ions **XI** from cation **III** under analogous conditions was observed by us previously [10]. Likewise, cation **II** was quickly con-

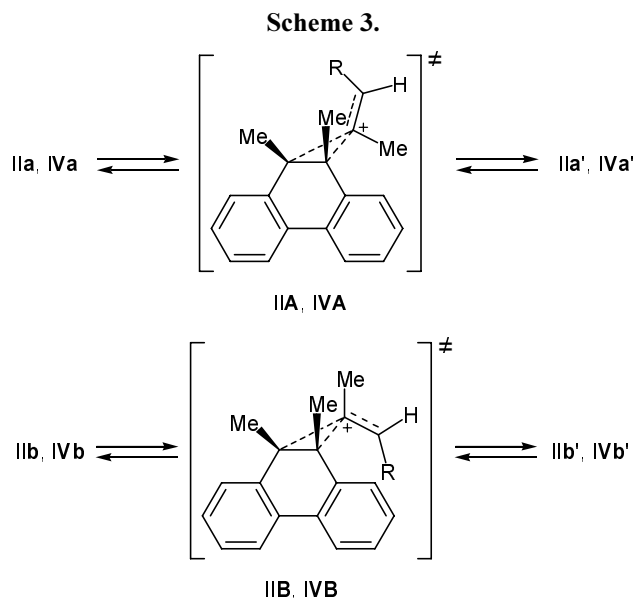
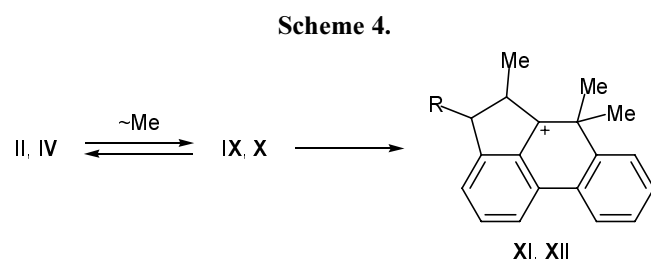


Table 3. Geometric parameters of transition states for degenerate rearrangements^a

Structure	Transition state						Initial state		
	conformation	l , Å	$v_{\text{CH}} - d_1$, Å	$v_{\text{HH}} - d_2$, Å	α_1 , deg	$180^\circ - \alpha_2$, deg	conformation	$v_{\text{CH}} - d_1$, Å	$v_{\text{HH}} - d_2$, Å
I	A	1.74	0.29	-0.04	95	1	a	0.10	-0.07
II	A	1.81	0.34	0.16	99	6	a	0.11	0.07
III	A	1.75	0.25	0.20	100	7	a	0.18	0.14
IV	B	1.75	0.37	0.24	109	12	b	0.16	0.01

^a l stands for the bond length connecting the migrating group and the cyclic skeleton; v_{CH} and v_{HH} are the sums of the van der Waals radii (2.87 and 2.32 Å, respectively [9]); d_1 is the shortest distance between the hydrogen atom in the R^3 (R^1) group and carbon atoms of the biphenyl fragment; and d_2 is the shortest distance between the hydrogen atoms in the R^1 (R^3) and 9(10)- CH_3 groups.

verted into 5,6,6-trimethyl-4,5,5a,6-tetrahydrocyclopenta[j,k]phenanthren-5a-yl cation (**XII**) above -80°C . Ion **XII** was also formed in the reaction of alcohol **V** with trifluoromethanesulfonic acid; the subsequent neutralization gave 5,6,6-trimethyl-4,6-dihydrocyclopenta[j,k]phenanthrene (**XIII**) (Scheme 4).



XI, R = Me; **XII**, R = H.

EXPERIMENTAL

The NMR spectra were recorded on Bruker AM-400 and AC-200 spectrometers (400.13 and 100.63 or 200.13 and 50.33 MHz for ^1H and ^{13}C , respectively). The chemical shifts were measured relative to the solvent signals (CD_2Cl_2 or CDCl_3 ; δ 5.33, 7.24, δ_{C} 53.3, 76.9 ppm, respectively). The temperature of the NMR probe was calibrated against the melting point of *n*-pentane (-130°C) and a standard sample of methanol (above 90°C); for intermediate temperatures, linear interpolation was used. The GC-MS data, high-resolution mass spectra, and IR spectra were obtained on Hewlett Packard G1800A, Finnigan MAT-8200, and Bruker Vector-22 instruments, respectively.

The syntheses were performed under argon. Tetrahydrofuran was preliminarily dried over potassium hydroxide, distilled over metallic sodium, and stored under argon. Fluorosulfonic acid was distilled twice (bp 158 – 161°C), SO_2ClF [11] was purified by passing

its vapor through concentrated sulfuric acid, CD_2Cl_2 was dried over 4-Å molecular sieves, and $\text{CF}_3\text{SO}_3\text{H}$ was commercial product (Aldrich).

Quantum-chemical calculations of the geometric parameters of carbocations and their proton chemical shifts were performed in terms of the density functional theory (DFT; PBE approximation) [12] using *Priroda* software [13] {triple zeta basis set; (11s6p2d)/[6s3p2d] for carbon and oxygen atoms and (5s1p)/[3s1p] for hydrogen atoms}. Exchange ^1H NMR spectra in the resonance region corresponding to CH_3 protons were calculated using MEX program [14].

9-Isopropenyl-10,10-dimethyl-9,10-dihydrophenanthren-9-ol (V). A solution of 3.86 g (17.4 mmol) of ketone **VIII** [5] in 8 ml of THF was added over a period of 1 h under stirring at room temperature to 25 ml of a solution of isopropenylmagnesium bromide, prepared from 3.00 g (24.8 mmol) of 2-bromoprop-1-ene (Aldrich) and 0.603 g (24.8 mmol) of magnesium in tetrahydrofuran. The mixture was heated for 1.5 h at 70°C , cooled to 0°C , slowly treated with 10 ml of a saturated aqueous solution of ammonium chloride, and extracted with hexane (3×20 ml). The extract was washed with a saturated aqueous solution of sodium chloride and dried over MgSO_4 , and the solvent was distilled off under reduced pressure. The residue, 4.17 g, was recrystallized from 5 ml of hexane to isolate 2.97 g (65%) of compound **V** containing 99% of the main substance (according to the GLC data). IR spectrum (CCl_4), ν , cm^{-1} : 3617 m, 3070 m, 2972 s, 2933 m, 1947 w, 1917 w, 1816 w, 1634 m, 1483 s, 1485 m, 1449 s, 1381 m, 1303 m, 1239 m, 1133 m, 1047 s, 996 s, 908 s. ^1H NMR spectrum (200 MHz, CDCl_3), δ , ppm: 1.13 s (3H, 10- CH_3), 1.21 d.d (3H, = CCH_3 , $J = 1.5, 0.7$ Hz), 1.42 s (3H, 10- CH_3), 2.06 s (1H, OH), 4.72 quint (1H, = CH_2 , $J = 1.6$ Hz), 5.17 d.q (1H, = CH_2 , $J = 1.7, 0.7$ Hz), 7.21–7.43 m (5H, H_{arom}),

7.55–7.67 m (1H, H_{arom}), 7.67–7.82 m (2H, H_{arom}). ¹³C NMR spectrum (50 MHz, CDCl₃), δ_C, ppm: 20.7 q (10-CH₃), 21.1 q (=CCH₃), 26.7 q (10-CH₃), 41.6 s (C¹⁰), 80.2 s (C⁹), 111.2 t (=CH₂), 122.8 d, 123.6 d, 124.1 d, 125.4 d, 126.7 d, 127.7 d, 128.2 d, 128.3 d, 132.8 s, 133.1 s, 140.5 s, 144.5 s, 148.2 s (=CCH₃). Found: *m/z* 264.1528 [*M*]⁺. C₁₉H₂₀O. Calculated: *M* 264.1514.

10,10-Dimethyl-9-(trans-1-methylprop-1-en-1-yl)-9,10-dihydrophenanthren-9-ol (VI). A solution of 3.97 g (29.4 mmol) of a mixture of monobromo derivatives (obtained by dehydrobromination of 2,3-dibromobutane according to the procedure recorded in [15] and purified by passing through a layer of calcined Al₂O₃) in 10 ml of THF was added over a period of 2 h to 0.706 g (29 mmol) of magnesium in 30 ml of THF under stirring at 50°C. The mixture was heated for 2 h under reflux, and a solution of 5.88 g (20 mmol) of ketone VIII [5] in 10 ml of THF was added over a period of 2 h to the resulting solution at room temperature. When the addition was complete, the mixture was heated for 2 h at 50°C, cooled to 0°C, slowly treated with 20 ml of a saturated aqueous solution of ammonium chloride, and extracted with 5 × 20 ml of hexane. The extract was washed with a saturated aqueous solution of sodium chloride and dried over Na₂SO₄, and the solvent was distilled off under reduced pressure to obtain 7.71 g of a multicomponent mixture of products. A 0.75-g portion of that mixture was subjected to chromatography on silica gel using hexane–diethyl ether (4:1) as eluent. From the first fraction (*R*_f 0.33) we isolated 0.265 g (49%) of a colorless oily liquid which was identified as alcohol VI (according to the NMR data). IR spectrum (CCl₄), ν, cm⁻¹: 3611 m, 3070 m, 2972 s, 1947 w, 1907 w, 1694 w, 1605 w, 1484 m, 1449 s, 1382 m, 1300 m, 1277 m, 1204 m, 1034 s. ¹H NMR spectrum (200 MHz, CDCl₃), δ, ppm: 1.26 quint (3H, =CCH₃, *J* = 1.4 Hz), 1.30 s (3H, 10-CH₃), 1.68 s (3H, 10-CH₃), 2.16 s (1H, OH), 2.19 d.q (3H, =CHCH₃, *J* = 7.4, 1.4 Hz), 5.77 q.q (1H, =CHCH₃, *J* = 7.4, 1.4 Hz), 7.34–7.60 m (5H, H_{arom}), 7.79–7.98 m (3H, H_{arom}). ¹³C NMR spectrum (50 MHz, CDCl₃), δ_C, ppm: 16.2 q.d (=CHCH₃, *J* = 126.6, 2.5 Hz), 21.4 q.q (10-CH₃, *J* = 126.6, 4.7 Hz), 24.5 q.d (=CCH₃, *J* = 126.4, 8.5 Hz), 26.0 q.q (10-CH₃, *J* = 127.5, 4.7 Hz), 42.9 m (C¹⁰), 83.1 m (C⁹), 122.4 d.m, 123.6 d.m, 123.7 d.m, 124.0 d.m, 126.0 d.m, 126.5 d.m, 127.6 d.m, 128.11 d.m, 128.14 d.m, 132.7 m, 133.1 m, 137.1 m, 141.5 m, 144.5 m. Found: *m/z* 278.1675 [*M*]⁺. C₂₀H₂₂O. Calculated: *M* 278.1671.

5,6,6-Trimethyl-4,6-dihydrocyclopenta[*j,k*]phenanthrene (XIII). A solution of 0.5 g (1.89 mmol) of alcohol V in 1.5 ml of chloroform was added dropwise under stirring at –60°C to 1.42 g (9.5 mmol) of trifluoromethanesulfonic acid. The dark crimson mixture was stirred for 15 min at room temperature, and the resulting solution was added dropwise over a period of 30 min under vigorous stirring to a suspension of 3.6 g of Na₂CO₃ in 70 ml of hexane containing 0.1 ml of methanol. The mixture was stirred for 30 min, water was added to dissolve Na₂CO₃, the organic phase was separated and filtered through a thin layer of Al₂O₃, and the solvent was distilled off under reduced pressure. The residue was 0.39 g (84%) of a crystalline substance which was identified as compound XIII with a purity of 98% (according to the GLC data). IR spectrum (CCl₄), ν, cm⁻¹: 3059 m, 2972 s, 2930 m, 1942 w, 1912 w, 1620 w, 1453 s, 1431 s, 1393 m, 1362 m, 1225 m, 1056 m, 1037 m. ¹H NMR spectrum (400 MHz, CDCl₃), δ, ppm: 1.71 s (6H, 6-CH₃), 2.33 s (3H, 5-CH₃), 3.36 s (2H, 4-H), 7.18 t (1H, 2-H, *J* = 7.7 Hz), 7.24–7.33 m (3H, 3-H, 8-H, 9-H), 7.54 d.d (1H, 7-H, *J* = 6.9, 2.3 Hz), 7.70 d (1H, 1-H, *J* = 7.9 Hz), 7.93 d.d (1H, 10-H, *J* = 6.9, 2.3 Hz). ¹³C NMR spectrum (100 MHz, CDCl₃), δ_C, ppm: 15.8 q (5-CH₃), 30.9 q (6-CH₃), 37.2 s (C⁶), 44.2 t (C⁴), 118.3 d, 121.8 d, 122.2 d, 124.5 d, 125.5 s, 126.1 d, 127.39 d, 127.42 d, 130.3 s, 136.3 s, 139.5 s, 140.6 s, 141.9 s, 145.7 s. Found: *m/z* 246.1417 [*M*]⁺. C₁₉H₁₈. Calculated: *M* 246.1400.

9-Isopropenyl-9,10-dimethylphenanthren-9-ylum (II) was generated from alcohol V in the system HSO₃F–SO₂ClF–CD₂Cl₂ by analogy with the procedure described in [2]. ¹H NMR spectrum (400 MHz, –107°C; for signal assignment, see Fig. 1), δ, ppm: 8.87–8.52 m (4H), 8.05–7.64 m (4H), 5.89 s (1H), 5.77 s (1H), 3.42 br.s (3H), 1.77 br.s (3H), 1.22 s (3H). ¹³C NMR spectrum (100 MHz), δ_C, ppm: 231.6 s, 149.4 s, 147.8 s, 142.4 s, 133.7 s, 127.2 s, 154.4 d, 137.5 d, 134.6 d, 131.1 d, 129.5 d, 128.1 d, 127.3 d, 126.1 d, 118.2 t, 63.9 s, 28.5 q, 24.6 q, 21.0 q.

5,6,6-Trimethyl-4,5,5a,6-trihydrocyclopenta[*j,k*]phenanthren-5a-ylum (XII) was generated either by heating a solution containing cation II in HSO₃F–SO₂ClF–CD₂Cl₂ to –30°C or from alcohol V in the system CF₃SO₃H–CDCl₃ by analogy with the procedure described in [8]. ¹H NMR spectrum (400 MHz, HSO₃F–SO₂ClF–CD₂Cl₂, –30°C), δ, ppm: 1.89 d (3H, 5-CH₃, *J* = 7.3 Hz), 1.98 s (3H, 6-CH₃), 2.02 s (3H, 6-CH₃), 3.39 d (1H, 4-H, *J* = 21.2 Hz), 3.98 d.d (1H,

4-H, $J = 21.2, 3.7$ Hz), 4.25 q.d (1H, 5-H, $J = 7.3, 3.7$ Hz), 7.74 t.d (1H, 9-H, $J = 7.6, 1.2$ Hz), 7.86 t.d (1H, 8-H, $J = 8, 1.2$ Hz), 7.90 d (1H, 3-H, $J = 7.1$ Hz), 8.03 d.d (1H, 7-H, $J = 8.2, 1.1$ Hz), 8.43 d (1H, 1-H, $J = 8.0$ Hz), 8.52 d.d (1H, 10-H, $J = 8.1, 1.2$ Hz), 8.66 t (1H, 2-H, $J = 7.7$ Hz). ^{13}C NMR spectrum (100 MHz, $\text{CF}_3\text{SO}_3\text{H}-\text{CDCl}_3, 20^\circ\text{C}$), δ_{C} , ppm: 241.0 m ($\text{C}^{5\text{a}}$), 169.2 m ($\text{C}^{3\text{a}}$), 155.4 d ($\text{C}^2, J = 161.7$ Hz), 150.2 m ($\text{C}^{6\text{a}}$), 145.9 d.d ($\text{C}^{10\text{b}}, J = 8.1, 4.2$ Hz), 139.5 t.q ($\text{C}^{10\text{c}}, J = 6.9, 2.2$ Hz), 134.0 d.d ($\text{C}^8, J = 165.1, 8.1$ Hz), 129.0 d.d ($\text{C}^9, J = 165.3, 7.4$ Hz), 127.2 d.d ($\text{C}^7, J = 159.8, 7.4$ Hz), 126.6 d.d.t (C^3 or $\text{C}^{10}, J = 160.9, 7.8, 1.0$ Hz), 126.5 d.d.t (C^{10} or $\text{C}^3, J = 170.2, 7.3, 2.3$ Hz), 126.4 m ($\text{C}^{10\text{a}}$), 122.8 d.d.d ($\text{C}^1, J = 165.3, 6.1, 2.5$ Hz), 50.7 d.m ($\text{C}^5, J = 130.3$ Hz), 50.7 m (C^6), 42.8 t.m ($\text{C}^4, J = 135.0$ Hz), 28.8 q.q (6- $\text{CH}_3, J = 132.9, 4.9$ Hz), 27.1 q.q (6- $\text{CH}_3, J = 133.5, 5.1$ Hz), 18.3 q.d.d (5- $\text{CH}_3, J = 131.2, 7.6, 3.8$ Hz).

A mixture of **9,10-dimethyl-9-(trans-1-methylprop-1-en-1-yl)phenanthren-9-ylium (IV)** and **10,10-dimethyl-9-(trans-1-methylprop-1-en-1-yl)phenanthren-9-ylium (X)** was generated from alcohol **VI** in the system $\text{HSO}_3\text{F}-\text{SO}_2\text{ClF}-\text{CD}_2\text{Cl}_2$ by analogy with the procedure described in [2]. The ^1H NMR spectra (400 MHz) of mixture **IV/X** were discussed above. ^{13}C NMR spectrum (100 MHz), δ_{C} , ppm: ion **IV**: 233.4 s, 151.9 s, 147.0 s, 134.3 s, 131.9 s, 126.1 s, 152.5 d, 136.8 d, 134.2 d, 131.0 d, 129.1 d, 128.3 d, 127.6 d, 127.1 d, 125.9 d, 62.4 s, 31.4 q, 25.7 q, 24.1 q, 14.4 q; **X**: 231.9 s, 150.1 s, 150.0 s, 134.2 s, 133.1 s, 126.9 s, 154.9 d, 141.2 d, 134.8 d, 131.8 d, 131.3 d, 129.2 d, 127.7 d, 126.8 d, 126.2 d, 54.4 s, 31.3 q, 28.8 q, 26.0 q, 16.5 q.

REFERENCES

1. Artamoshkin, V.G., Bushmelev, V.A., Genaev, A.M., and Shubin, V.G., *Mendeleev Commun.*, 2006, p. 112.
2. Bushmelev, V.A., Genaev, A.M., and Shubin, V.G., *Russ. J. Org. Chem.*, 2006, vol. 42, p. 100.
3. Bushmelev, V.A., Genaev, A.M., and Shubin, V.G., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2004, p. 2767.
4. Bushmelev, V.A., Genaev, A.M., and Shubin, V.G., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 966.
5. Zincke, T. and Tropp, W., *Justus Liebigs Ann. Chem.*, 1908, vol. 362, p. 242.
6. Beach, W.F. and Richards, J.H., *J. Org. Chem.*, 1961, vol. 26, p. 3011.
7. Koptug, V.A., *Arenonievye iony. Stroenie i reaktivnaya sposobnost'* (Aryl Cations. Structure and Reactivity), Novosibirsk: Nauka, 1983.
8. Rezvukhin, A.I., Korchagina, D.V., and Shubin, V.G., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, p. 1253.
9. Zefirov, Yu.V. and Zorkii, P.M., *Zh. Strukt. Khim.*, 1974, vol. 15, p. 118.
10. Bushmelev, V.A., Genaev, A.M., Osadchii, S.A., Shakirov, M.M., and Shubin, V.G., *Russ. J. Org. Chem.*, 2003, vol. 39, p. 1301.
11. Woyski, M.M., *J. Am. Chem. Soc.*, 1950, vol. 72, p. 919.
12. Perdew, J.P., Burke, K., and Ernzerhof, M., *Phys. Rev. Lett.*, 1996, vol. 77, p. 3865.
13. Laikov, D.N., *Chem. Phys. Lett.*, 1997, vol. 281, p. 151; Laikov, D.N. and Ustynyuk, Yu.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2005, p. 804.
14. Bain, A.D. and Duns, G.J., *Can. J. Chem.*, 1996, vol. 74, p. 819.
15. Bordwell, F.G. and Landis, P.S., *J. Am. Chem. Soc.*, 1957, vol. 79, p. 1593.