

Degenerate Rearrangement of Long-Lived 9,10-Dimethyl-9-(*cis*-1-methyl-1-propenyl)phenanthrenium Ion: 1,2-Shift of the Dimethylvinyl Group*

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Abstract—Dynamic NMR study showed that 9,10-dimethyl-9-(*cis*-1-methyl-1-propenyl)phenanthrenium ion generated by reaction of 1,2,2a,10b-tetramethyl-2a,10b-dihydrocyclobuta[1]phenanthrene with HSO_3F below -100°C undergoes very fast ($\Delta G^\ddagger = 22$ kJ/mol at -120°C) degenerate 1,2-shift of the dimethylvinyl group.

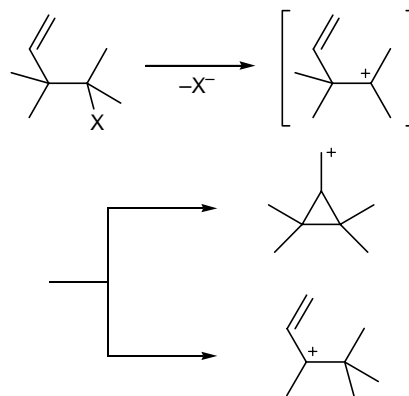
An approach developed by V.A. Koptug and his disciples [2] is very fruitful for quantitative description of cationoid rearrangements. This approach implies building up of such model carbocationic structures which could be generated under conditions ensuring their long lifetime and could be divided mentally into two interacting structural fragments, migrating group and framework [3]. Of specific interest are carbocations which can be detected by physical methods and are capable of undergoing degenerate rearrangements involving 1,2-shift of the migrating group. Kinetic studies of these rearrangements give information on “internal barriers” intrinsic to common (i.e., nondegenerate) rearrangements, which is necessary to predict their rate [4].

Up to now, numerous kinetic data have been obtained for carbocationic rearrangements involving 1,2-shift of various migrating groups, including hydrocarbon ones [5]. However, we have found no published data on rearrangements occurring via 1,2-shift of a vinyl or substituted vinyl group in long-lived carbocations. An example of such transformation, reported in [6], refers to a cationic structure which cannot be divided into migrating group and framework; moreover, it was not confirmed by the subsequent study of the same authors [7].

Ionization of compounds of the benzocycloalkene series, which are potential precursors of β -vinyl-substituted carbocations, by the action of superacids

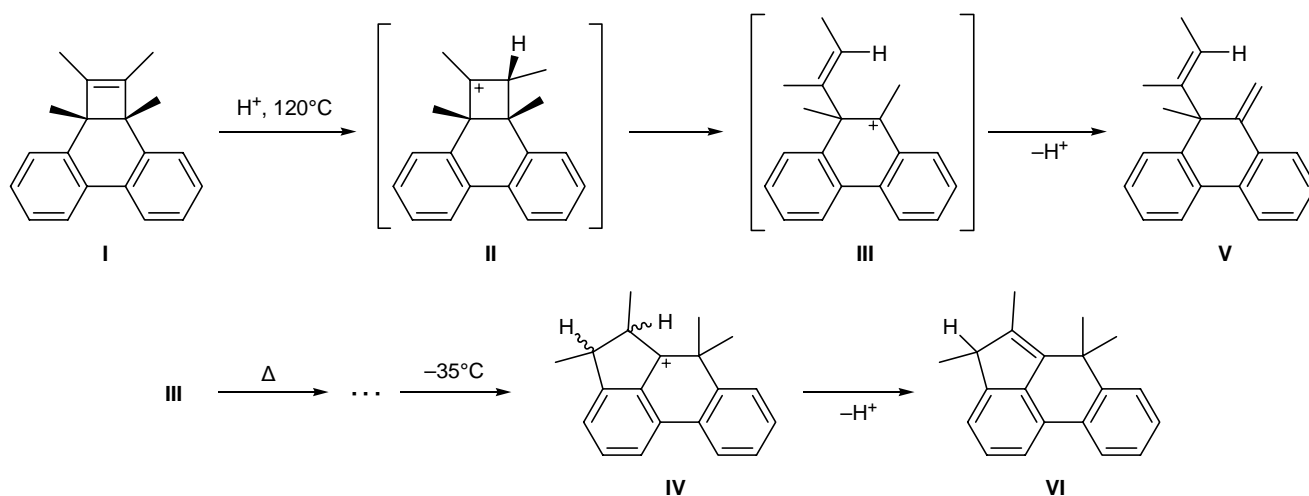
usually produces either nonclassical homoallyl carbocations or products of their rearrangements [8]. Those β -vinyl-substituted carbocations which can be detected by NMR spectroscopy (when an effective electron-donor substituent is present in the α -position with respect to the cationic center) do not tend to undergo rearrangements via vinyl shift [8]. Ionization of potential precursors of long-lived β -vinyl-substituted carbocations of the aliphatic series leads to formation of allyl- and cyclopropylcarbinyl cations due to effective interaction between the emerging carbocationic center and the vinyl group [9, 10] (Scheme 1). A similar pattern was observed with β -phenyl-substituted carbocations: the relative migrating ability of phenyl and substituted phenyl groups was determined for the first time using 9-aryl-9,10-dimethylphenanthrenium ions as structural model [11]. We anticipated

Scheme 1.



* For preliminary communication, see [1].

Scheme 2.



that the model based on 9-substituted 9,10-dimethylphenanthrenium ions, where the positive charge is delocalized over the aromatic ring, will also be useful for estimation of the migrating ability of vinyl and substituted vinyl groups.

In this connection, the results obtained by us while studying the behavior of 1,2,2a,10b-tetramethyl-2a,10b-dihydrocyclobuta[l]phenanthrene (**I**) in superacids [12] were especially interesting. We found that compound **I** in the acid system $HSO_3F-SO_2ClF-CD_2Cl_2$ (1:4:1, by volume) undergoes rearrangement to give a mixture of *cis*- and *trans*-4,5,6,6-tetramethyl-4,5,6-trihydrocyclopenta[*j,k*]phenanthren-5-yl cations **IVa** and **IVb**. Here, 9,10-dimethyl-9-(*cis*-1-methyl-1-propenyl)phenanthrenium ion (**III**) was assumed to be one of the primary intermediates. This assumption was based on the formation of 9-methyl-10-methylene-9-(*cis*-1-methyl-1-propenyl)-9,10-dihydrophenanthrene (**V**) in a mixture with olefin **VI** (Scheme 2) upon neutralization of the acid solution at $-100^\circ C$.

The goal of the present work was to confirm the formation of cation **III**, reveal degenerate rearrangement of cation **III** via 1,2-shift of the dimethylvinyl group, and estimate the rate of this process.

Dissolution of compound **I** in $HSO_3F-SO_2ClF-CD_2Cl_2$ (1:4:1, by volume) at $-130^\circ C$ gave a mixture whose 1H NMR spectrum (recorded at $-109^\circ C$) contained three signals belonging to methyl protons (a broad six-proton singlet at δ 2.54 ppm, a doublet at δ 1.95 ppm, and a singlet at δ 1.06 ppm), four signals in the region δ 7.8–8.8 ppm (two doublets and two triplets, 2H each) from aromatic protons, and a quartet from a single proton at δ 6.42 ppm with a coupling

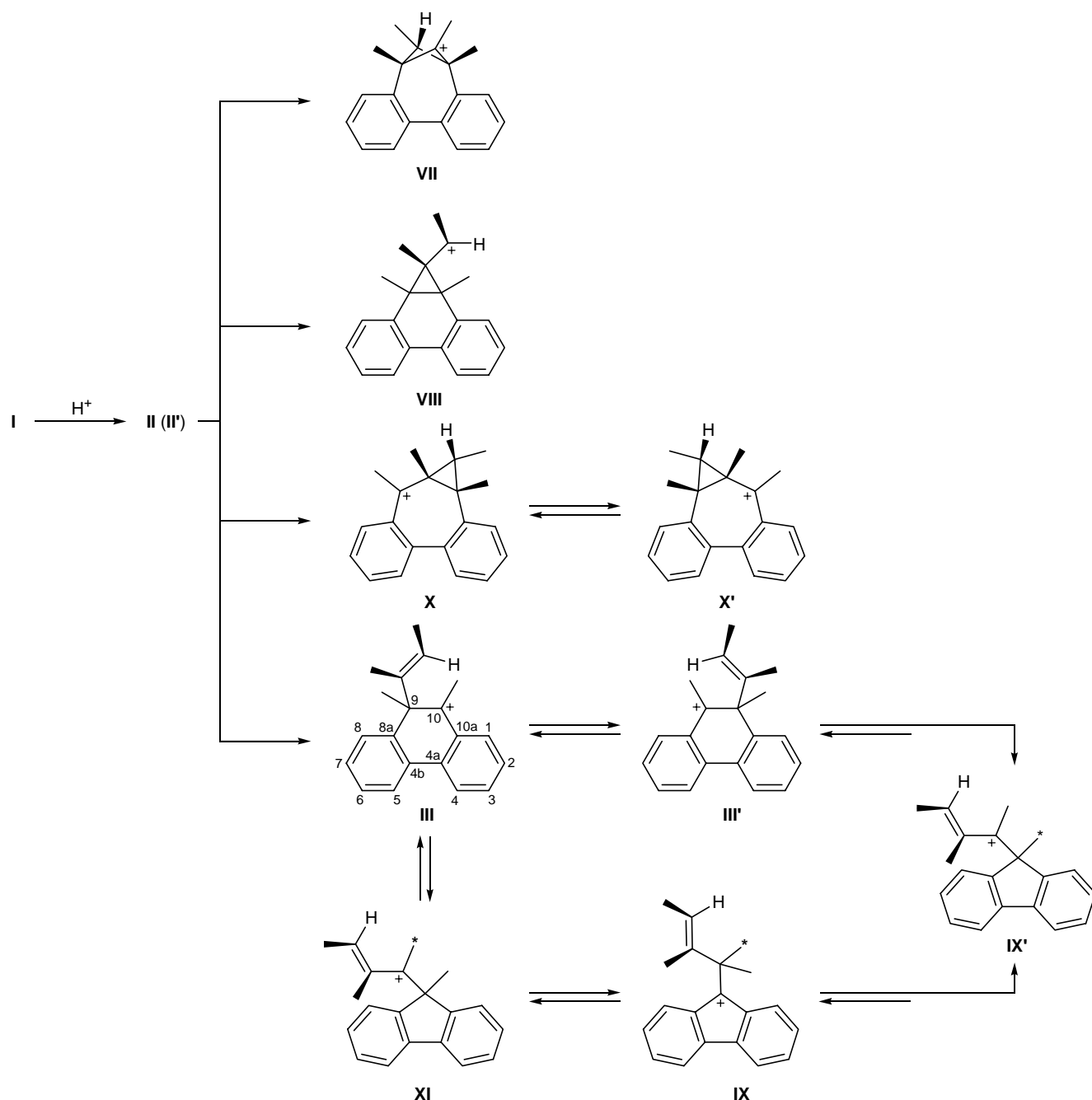
constant of 7 Hz. Obviously, the latter signal belongs to a proton neighboring to the methyl group which gives the doublet signal. Formally, the above 1H NMR spectral pattern may originate from either a species possessing a symmetry plane (in particular, cation **VII** [13], **VIII**, or **IX**) or a dynamic system consisting of two species (**III** \rightleftharpoons **III'**, **X** \rightleftharpoons **X'**, or **XI** \rightleftharpoons **XI'**) which are involved in fast (on the NMR time scale) degenerate rearrangement. This process leads to averaging of signals from two of the four methyl groups and respective pairs of aromatic protons (Scheme 3).** Obviously, the dynamic system **II** \rightleftharpoons **II'** which could be generated by protonation of olefin **I** should be excluded from consideration: In the case of degenerate interionic or intermolecular (through the medium) 1,2-migration of hydrogen in cyclobutyl cation **II**, only two six-proton signals from the methyl groups would be observed in the averaged spectrum.

The number of stereoisomeric carbocations which could be formed from cation **II** is limited by stereoselectivity of the protonation of olefin **I** (from the *exo* side) [12] and by the impossibility for *antara*-migration of carbon–carbon bonds in small rings [14]. Possible structures are shown in Scheme 3.

Comparison of the experimental 1H NMR spectrum with that calculated *ab initio* (Fig. 1, Table 1) led us to presume that it corresponds to the dynamic system **III** \rightleftharpoons **III'**. Here, we did not take into account signals from the aromatic protons. The calculated chemical shifts of the aromatic protons in *cis*- and *trans*-**IV** [12],

** These cations can be formed from ion **II** via processes typical of carbocations, i.e., 1,2-shift or cleavage of the β -C–C bond.

Scheme 3.



4-(2-biphenyl)-1,2,3,4-tetramethylcyclobutenyl cation (**XII**) [12], and 4,5,9,9,10-pentamethylphenanthrenium cation (**XIII**) [15] showed a poor agreement with the experimental data. The differences between the calculated and experimental chemical shifts of the other protons (see footnote ^b to Table 1) for cations *cis*-**IV**, *trans*-**IV**, **XII**, and **XIII** were 0.34, 0.22, 0.08, and 0.11 ppm, respectively. As follows from the data in Table 1, the best agreement with the experimental spectrum was observed for one conformer of **III**

(**IIIa**, Fig. 1), which turned out to be the most stable among the other species given therein. Presumably, the upfield position of signal from one methyl group in the dimethylvinyl fragment (δ 1.06 and 1.34 ppm in the experimental and calculated 1H NMR spectrum of **III**, respectively) results from anisotropic effect of the neighboring aromatic ring.

An additional support to the presumed dynamic system $III \rightleftharpoons III'$ was obtained by comparing the experimental 1H NMR spectrum with those reported in

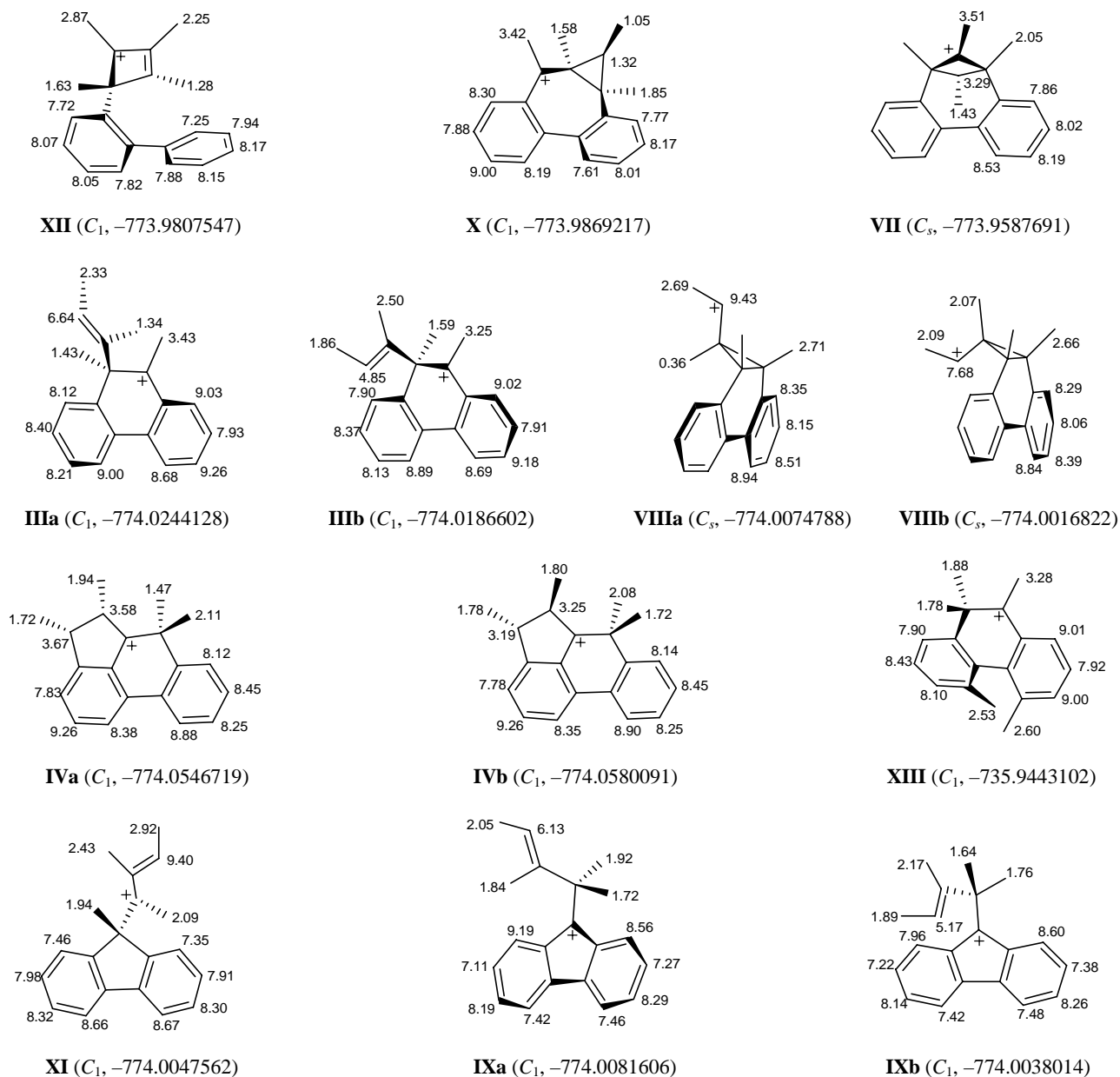


Fig. 1. Calculated structures and proton chemical shifts (δ , ppm) of cations **III**, **IV**, and **VII–XIII**; in parentheses are given the symmetry groups and total energies (a.u.).

[4] for degenerate rearrangements of 9-R-9,10-dimethylphenanthrenium ion via 1,2-shift of the group R. For example, the differences in the chemical shifts of the aromatic protons (averaged in pairs) in cation **III** and 9,10-dimethyl-9-phenylphenanthrenium ion (**XIV**) (1,2-Ph shift [11]) are 0.12, 0.03, -0.02, and -0.03 ppm for 1-H/8-H, 2-H/7-H, 3-H/6-H, and 4-H/5-H, respectively.

The ^{13}C NMR spectra are also consistent with formation of dynamic carbocation system $\mathbf{III} \rightleftharpoons \mathbf{III}'$ on protonation of compound **I**. The spectrum recorded

at -120 to -109°C contained a set of averaged signals, which was analogous to that observed for the degenerate rearrangement of ion **XIV** [16] (Fig. 2). In both cases, no signal from C^9/C^{10} was detected, presumably because of a large difference in the chemical shifts of these atoms [15].

Let us consider possible mechanisms of the degenerate rearrangement of cation **III**. The most probable is that involving 1,2-shift of the dimethylvinyl group (Scheme 3). Reversible 1,2-shifts of methyl groups, as shown in Scheme 4, can be ruled out on the basis of

Table 1. Experimental and calculated proton chemical shifts and relative stabilities of cations **III** and **VII–XI**

Cation no. ^a	Chemical shift δ , ppm				Deviation ^b	Relative stability, ^c kJ/mol
	s (3H)	d (3H)	s (6H)	q (1H)		
Experimental	1.06	1.95	2.54	6.42		
IIIa	1.34	2.33	2.43	6.64	0.27	-89.5
IIIb	2.50	1.86	2.42	4.85	1.07	-74.5
VII	3.51	1.43	2.05	3.29	2.02	82.8
VIIIa	0.36	2.69	2.71	9.43	1.59	-44.8
VIIIb	2.09	2.07	2.66	7.68	0.82	-29.7
IXa	1.84	2.05	1.82	6.13	0.55	-46.9
IXb	2.17	1.89	1.70	5.17	0.94	-35.1
X	1.58	1.05	2.64	1.32	2.60	9.2
XI	2.43	2.92	2.01	9.40	1.73	-37.7

^a For conformer structure, see Fig. 1.

^b Square root of the average squared difference between the calculated and experimental value.

^c The energy of cation **II** was taken as zero level.

the averaged ¹³C NMR spectrum (Fig. 2) and the presence of averaged signals from aromatic protons in the ¹H NMR spectrum. A more complex mechanism involving intermediate formation of fluorene-based

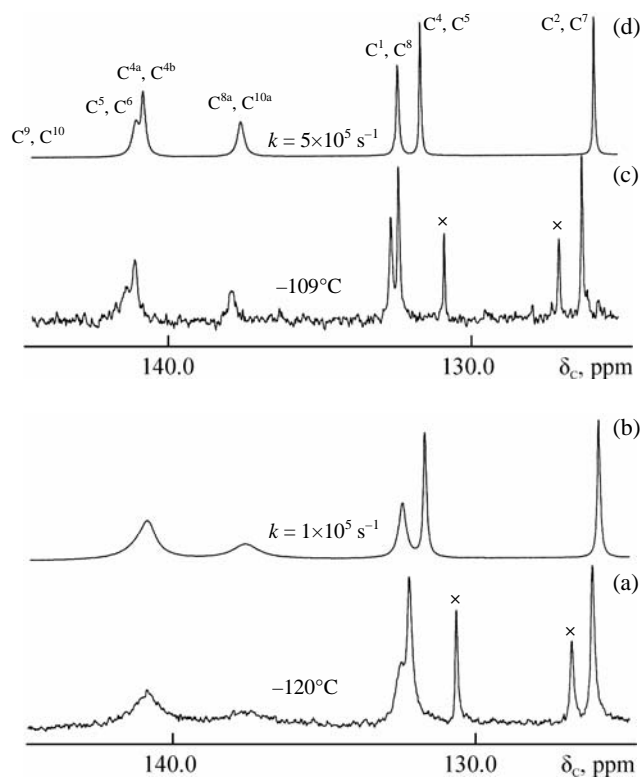
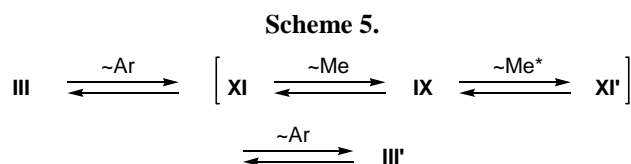
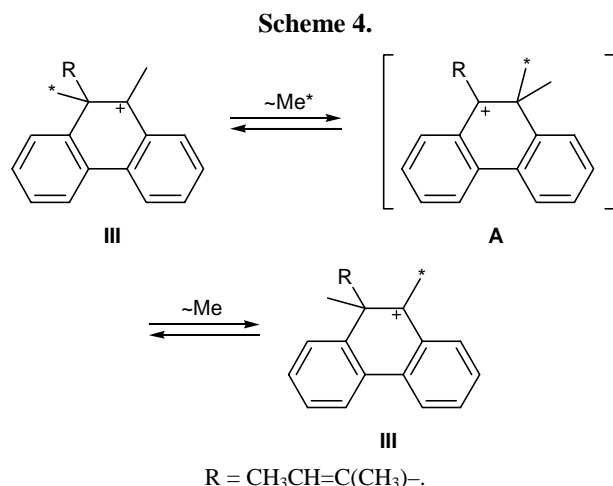


Fig. 2. ¹³C NMR spectra of cation **III**: (a, c) experimental spectra (signals from carbon atoms at the double bond in the migrating group are indicated by crosses) and (b, d) spectra calculated for the given migration rate constants.

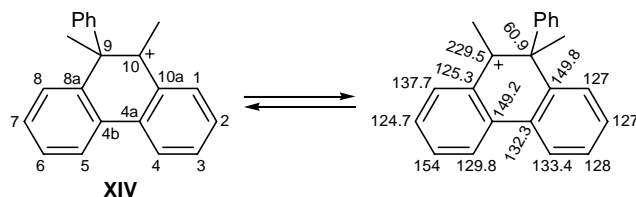
cations (Scheme 5) [15, 17] is also hardly probable, for in this case no averaging of the C⁹ and C¹⁰ signals would be observed. Mechanisms involving intermediate formation of cations **II**, **VII**, and **X**, e.g., **III** \rightleftharpoons (**II** \rightleftharpoons **VIII** \rightleftharpoons **II'**) \rightleftharpoons **III'** or **III** \rightleftharpoons (**II** \rightleftharpoons **X** \rightleftharpoons **VII** \rightleftharpoons **X'** \rightleftharpoons **II'**) \rightleftharpoons **III'**, can be excluded taking into account that the energies of cations **II**, **VII**, and **X** (Table 1) are much higher than the energy of the transition state in the degenerate rearrangement of cation **III** (see below).

Therefore, we conclude that cation **III** undergoes degenerate rearrangement via 1,2-sigmatropic shift of



the dimethylvinyl group. The rate of the rearrangement was estimated by dynamic ^{13}C NMR (Fig. 2). The chemical shifts necessary for the calculation (in the absence of exchange) were assumed to be equal to those found for 9,10-dimethyl-9-phenylphenanthrenium ion (**XIV**) [16] (Scheme 6) since we failed to obtain spectra of the “frozen” form. Ion **XIV** is a close structural analog of **III**, where the substituent at C^9 is phenyl rather than dimethylvinyl group. According to the data of [16], substituent at C^9 only slightly affects chemical shifts of carbon nuclei in the phenanthrene fragment of such cations. The rate of the degenerate rearrangement of cation **III** was very high even at -120°C ($k = 1 \times 10^5 \text{ s}^{-1}$, $\Delta G^\ddagger = 22 \text{ kJ/mol}$). The migrating ability of the dimethylvinyl group considerably exceeds that of other hydrocarbon groups (Table 2), which may be due to effective participation of the double bond in delocalization of the positive charge in the transition state.

Scheme 6.



Raising the temperature of a solution containing cation **III** above -100°C leads to decrease in the intensity of its signals in the ^1H NMR spectrum and appearance of signals belonging to other species. Presumably [12], this is the result of irreversible 1,2-Me shift in cation **III**; the rate of this process ($k = 3.4 \times 10^{-4} \text{ s}^{-1}$ at -109°C , $\Delta G^\ddagger = 50.3 \text{ kJ/mol}$) is much lower than the rate of degenerate rearrangement of **III**. However, contrary to the expectations [12], it differs only slightly from the rate of 1,2-Me shift in 9,9,10-trimethylphenanthrenium ion **XV** (Table 2) [17]. This casts some doubt on the considerable extent of homoallyl interaction between the double bond and carbocationic center in ion **III**.

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EXPERIMENTAL

The NMR spectra were recorded on a Bruker AM-400 spectrometer using the signals of CD_2Cl_2 as reference (δ 5.33, δ_{C} 53.3 ppm). The temperature of the probe was calibrated against the melting point of

Table 2. Gibbs energies of activation for 1,2-shift of migrating groups R in degenerate rearrangements of 9-R-9,10-dimethylphenanthrenium ions [5]

R	ΔG^\ddagger , ^a kJ/mol
CH_3	48.7
CH_3CH_2	42.3 (25°C)
$\text{CH}_2=\text{CHCH}_2^{\text{b}}$	33.9 (-90°C)
$\text{C}_6\text{H}_5\text{CH}_2^{\text{c}}$	36.0
C_6H_5	39.4

^a Recalculated to -120°C unless otherwise stated.

^b 3,6-Dibromo derivative.

^c 3,6-Dimethyl derivative.

n-pentane (-130°C) and a standard sample of methanol (-90°C). Intermediate temperatures were set by linear interpolation.

Fluorosulfonic acid was distilled twice (bp $158\text{--}161^\circ\text{C}$), SO_2ClF [18] was dried by passing its vapor through concentrated sulfuric acid, and CD_2Cl_2 was dried over 4-Å molecular sieves.

Quantum-chemical calculations of the structures of carbocations were performed at the Novosibirsk State University using GAMESS software [19] with the B3LYP/6-31G* basis set. The chemical shifts (Fig. 1) were calculated with the IGLO-II basis set [20] using DALTON software [21]. The exchange NMR spectra were calculated using MEX program [22] built in xsim package [sm. ftp://nmr.nioch.nsc.ru/pub/nmr/].

9,10-Dimethyl-9-(*cis*-1-methyl-1-propen-1-yl)-phenanthrenium fluorosulfonate (III**).** An NMR ampule was charged with 225 mg (2.25 mmol) of HSO_3F . The ampule was cooled to -90°C , 0.15 ml of SO_2ClF was added, and the mixture was stirred. An additional portion of SO_2ClF , 0.05 ml, was then added as a separate layer. The ampule was immersed into a Dewar bottle containing frozen pentane (-130°C), and a suspension of 20–40 mg (0.08–0.15 mmol) of compound **I** [12, 23] in 0.2 ml of SO_2ClF and 0.1 ml of CD_2Cl_2 was added to the ampule. After 5 min, the mixture was stirred (with a glass rod cooled with liquid nitrogen) over a period of 30 min until it became a light red transparent solution. ^1H NMR spectrum, δ , ppm (-109°C): 1.06 s [3H, C(Me)CHMe], 1.95 d [3H, C(Me)CHMe, $J = 7 \text{ Hz}$], 2.54 br.s (6H, 9-Me, 10-Me), 6.42 q [1H, C(Me)CHMe, $J = 7 \text{ Hz}$], 7.88 (2H, 2-H, 7-H, $J = 8 \text{ Hz}$), 8.20 t (2H, 3-H, 6-H, $J = 8 \text{ Hz}$), 8.71 d (2H, 4-H, 5-H, $J = 8 \text{ Hz}$), 8.26 d (2H, 1-H, 8-H, $J = 8 \text{ Hz}$). ^{13}C NMR spectrum, δ_{C} , ppm (-109°C): 13.0, 15.3 [C(Me)CHMe]; 25.9 (9-Me, 10-Me); 126.3,

127.1, 130.8, 132.4, 132.6, 137.8, 141.0, 141.4 (C_{arom} , for detailed assignment, see Fig. 2; no averaged signal from C^9 and C^{10} was observed).

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