

# Rearrangements of 1-(1-Methylprop-1-en-1-yl)-1,2-dimethylacenaphthylenonium Ions

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**Abstract**—It was discovered by means of dynamic NMR that the 1-(*cis*-1-methylprop-1-en-1-yl)-1,2-dimethylacenaphthylenonium ion generated under conditions of “long life” for carbocations underwent fast ( $\Delta G^\ddagger$  35.8 kJ mol<sup>-1</sup> at -103°C) degenerate 1,2-shift of the *cis*-dimethylvinyl group. Quantum-chemical calculations by DFT method predict lower rate of 1,2-shift for the *trans*-dimethylvinyl group compared to *cis*-dimethylvinyl group and dependence on the cations conformation of the rates of these processes and of the rearrangement mechanism into the ions of phenalenyl type.

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We established in [1] by NMR method that the protonation of 1,2,2a,10b-tetramethyl-2a,10b-dihydrocyclobuta[1]phenanthrene (**I**) with fluorosulfonic acid at low temperature resulted in “observable” 9-(*cis*-1-methylprop-1-en-1-yl)-9,10-dimethylphenanthrenonium ion (**II**) which suffered very fast degenerate 1,2-shifts of dimethylvinyl group (Scheme 1).

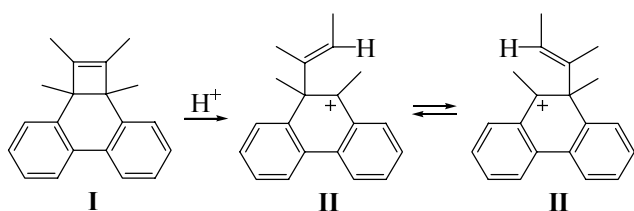
The discovery of this rearrangement was the first instance of “direct observation” of the vinyl shift in the carbocationic rearrangements. It is of considerable interest to establish the dependence of these processes rate on the structure of the skeleton of the carbocations undergoing the rearrangement. It was formerly found by an example of degenerate rearrangements occurring by 1,2-shifts of various migrating groups that the corresponding rates varied in a very wide range with alteration of the skeleton [2], and the characteristic rearrangement rates for 1-R-1,2-dimethylacenaphthylenonium ions were much slower than those for 9-R-9,10-dimethylphenanthrenonium ions. For instance in going from

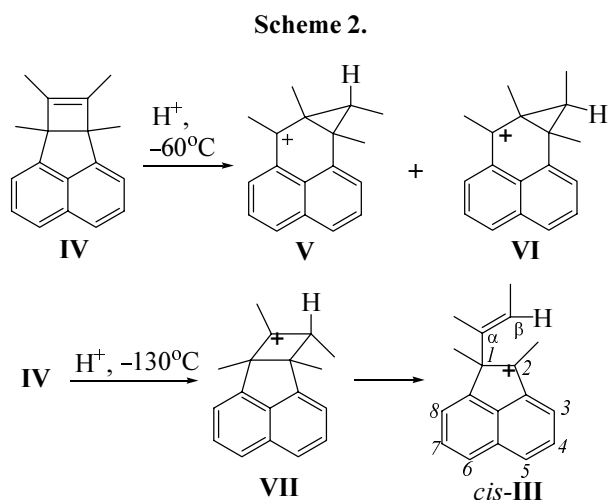
9,9,10-trimethylphenanthrenonium cation to 1,1,2-trimethylacenaphthylenonium ion the free energy of activation for the 1,2-shift of the methyl group grew from 48 to 77 kJ mol<sup>-1</sup>. Therefore it appeared sensible to generate the “observable” 1-(*cis*-1-methylprop-1-en-1-yl)-1,2-dimethylacenaphthylenonium ion *cis*-(**III**) and to reveal its degenerate rearrangement occurring by the 1,2-shift of the dimethylvinyl group in order to compare the rearrangement rate with that of cation **II**.

We believed that analogous to cation **II** cation *cis*-**III** could be generated by treating at low temperature with fluorosulfonic acid 6b,7,8,8a-tetramethyl-6b,8a-dihydrocyclobuta[*a*]acenaphthylene (**IV**) [3, 4] (Scheme 2). According to [4] this reaction at -60°C afforded a mixture of cations: 3b,4-*endo*,4a,5-tetramethyl-3b,4,4a,5-tetrahydro-4*H*-cyclopropa[*a*]-phenalen-5-yl (**V**) and its *exo*-epimer **VI**. Therefore we decided to carry out this reaction at lower temperature.

It was found that mixing of the solution of hydrocarbon **IV** in CD<sub>2</sub>Cl<sub>2</sub> with the fluorosulfonic acid diluted with SO<sub>2</sub>ClF even at -130°C as showed the <sup>1</sup>H NMR spectra resulted in a mixture of carbocations with cation **V** prevailing (93%). Besides the signals of this cation the spectrum contained also the signals of the minor epimer **VI** (2%). These species were identified by comparing the observed <sup>1</sup>H NMR spectra with those published in [4].

Scheme 1.



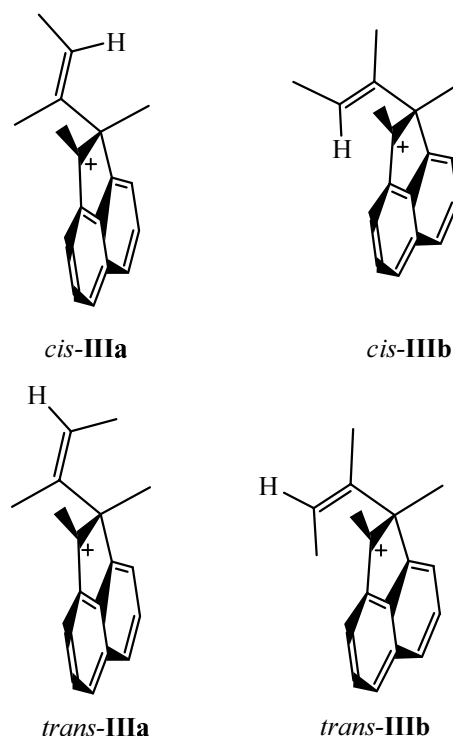


However alongside the signals from cations **V** and **VI** the spectrum contains also the signals with the following chemical shifts ( $\delta$ , ppm,  $-120^\circ\text{C}$ ) and intensities (in parentheses): 1.77 br. s (3H), 1.01 s (3H), 1.89 d (3H,  $J$  6 Hz), 6.31 q (1H,  $J$  6 Hz) and 9.02 (1H), 9.33 (1H). On the grounds of comparison with the  $^1\text{H}$  NMR spectra of 1-R-1,2-dimethylacenaphthylenonium ions (R = Me [5], Et [6]) and with the spectrum of cation **II** we concluded that these signals correspond respectively to the 1- $\text{CH}_3$ ,  $\alpha$ - $\text{CH}_3$ ,  $\beta$ - $\text{CH}_3$  groups, to the H atom of the 1- $\text{C}(\text{CH}_3)=\text{CHCH}_3$  moiety, and to the protons  $\text{H}^3$  and  $\text{H}^5$  of cation **III**. The other signals of this cation are overlapped by strong resonances of cation **V**. The abnormally high upfield chemical shift of the  $\alpha$ - $\text{CH}_3$  group from the dimethylvinyl fragment (1.01 ppm) is apparently due to the anisotropic effect of the aromatic skeleton.

With raising temperature of the sample from  $-120$  to  $-91^\circ\text{C}$  the content of cation **III** decreased from 5 to 0%, and simultaneously grew the amount of cation **VI** (from 2 to 7%); the percent of cation **V** therewith remained unchanged (93%). According to the rate of decrease in the intensity of cation **III** signals (1.2 times in 30 min at  $-114^\circ\text{C}$ ) the energy barrier to its conversion into cation **VI** is  $50 \text{ kJ mol}^{-1}$ . At further heating the reaction mixture up to  $-30^\circ\text{C}$  the ratio of cations **V** and **VI** is retained. The rearrangement of cation **V** into **VI** was shown [4] to occur only at the room temperature. This fact rules out the formation of cation **VI** at low temperature along the route  $\text{III} \rightleftharpoons \text{V} \rightleftharpoons \text{VI}$ .

Let us consider the structure of cation **III** in more detail. As follows from the quantum-chemical calculations each possible configuration of dimethylvinyl group corresponding to cations *cis*-**III** and *trans*-**III** may exist in two conformations, **IIIa** and **IIIb**, which appear as

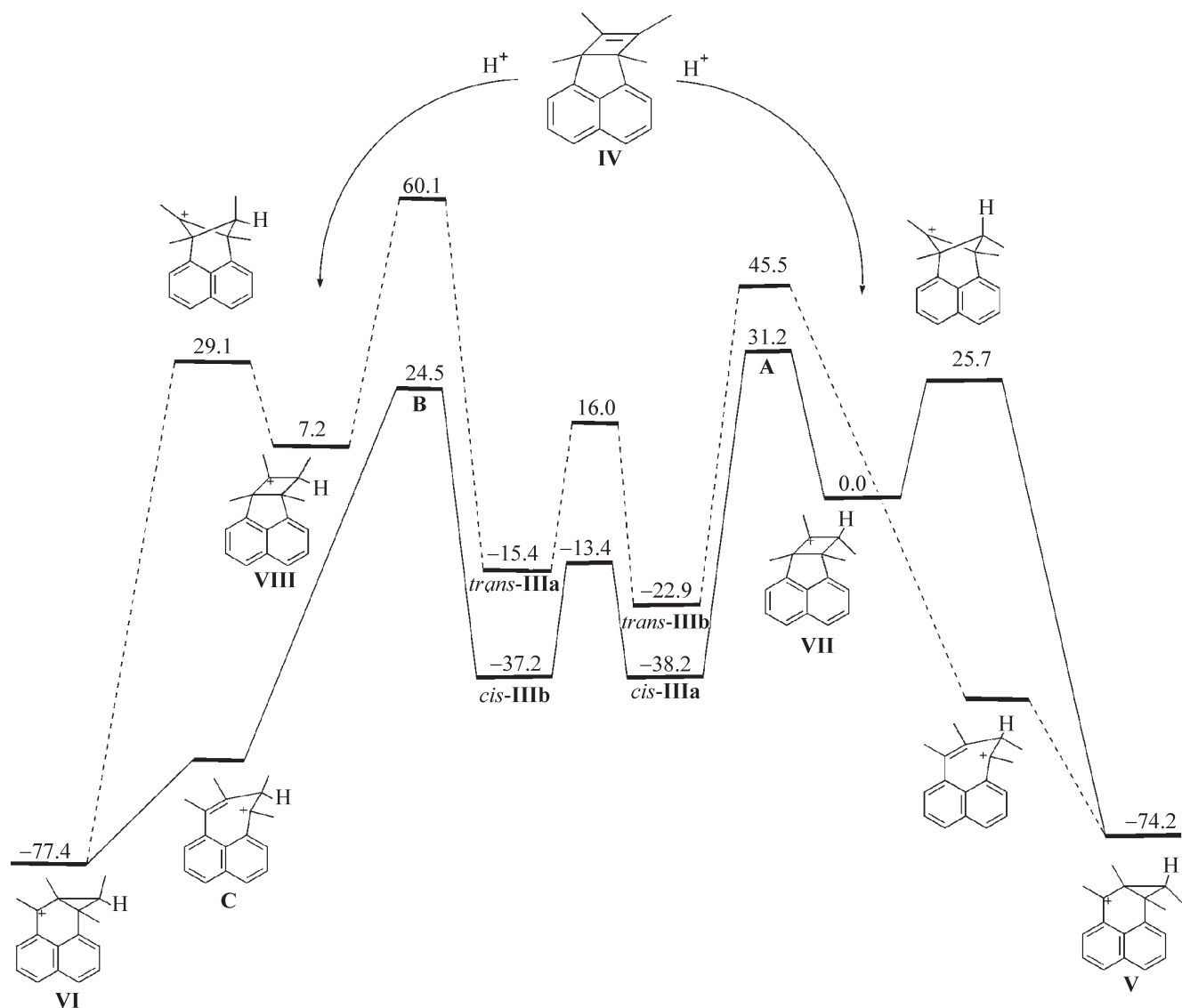
the respective minima on the potential energy surface (PES) (see the figure).



Significant deviations of calculated chemical shifts in the  $^1\text{H}$  NMR spectra (Table 1) from the experimental findings make it possible to rule out the structures *cis*-**IIIb** and *trans*-**IIIb**. Among the rest structures *cis*-**IIIa** should be preferred for its calculated chemical shifts are closer to the experimental data. Besides, the calculations show that the structure *trans*-**IIIa** is less stable than *trans*-**IIIb**, and the barrier to transition of the former into the latter is low (see the figure), therefore the experimental observation of the structure *trans*-**IIIa** seems hardly probable.

But these statements contradict the above cited experimental data which show that cation **III** transforms into ion **VI** and not into epimer **V**. The findings would suggest that in the generated cation **III** the dimethylvinyl group possesses a *trans*-configuration. It is really a logical assumption that cation **VI** forms exclusively from ion **VIII**, a product of a proton addition to hydrocarbon **IV** from the *endo*-side [4], but not from the *exo*-epimer **VII**; therewith the cyclization of cation **III** into **VIII** allowed by the Woodward–Hoffmann rule [7] anticipates the *trans*-configuration of the dimethylvinyl group (cf. data from [1, 8]).

However, the conclusion on cation *trans*-**III** formation would be erroneous: it is not consistent with the calculated

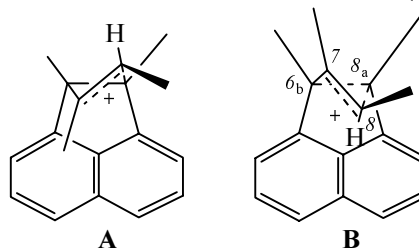


The calculated energy profile of the carbocation rearrangements. Arabic numerals correspond to the relative values of the respective energy levels ( $\text{kJ mol}^{-1}$ ).

PES profile (see the figure) which suggests that cation **VIII** should transform into cation **VI** and not into cation *trans*-**III**. Note also that the calculated barrier for the rearrangement of cation *trans*-**III** into cation **VI** equals  $83.0 \text{ kJ mol}^{-1}$ , significantly exceeding the experimental value for the rearrangement **III**→**VI** ( $50 \text{ kJ mol}^{-1}$ ).

This contradiction was removed by the detailed investigation of the cyclization pathways of “a” and “b” conformations of cation **III** which revealed previously unknown routes of rearrangement of **III** type cations into cations **V** and **VI** (see the figure) not involving intermediates **VII** and **VIII** (cf. [4]). It was found that the approach of the  $\beta$ -carbon from the dimethylvinyl group to the carbocation center in the conformation *cis*-**IIIa**

led to the transition state **A**, and the “descent” therefrom by procedure IRC (Intrinsic Reaction Coordinate) furnished cation **VII**. In case of cation *cis*-**IIIb** formed the transition state **B\*** located lower (the barrier to



\* The numbering of atoms used corresponds to hydrocarbon **IV**. Here and hereinafter the pictures of the activated complexes are projections of the calculated structures.

**Table 1.** Observed and calculated chemical shifts,  $\delta$ , ppm

Cation	Signals											Deviation <sup>a</sup>
	$\alpha$ -CH <sub>3</sub>	$\beta$ -CH <sub>3</sub>	H <sup><math>\beta</math></sup>	1-CH <sub>3</sub>	2-CH <sub>3</sub>	H <sup>3</sup>	H <sup>4</sup>	H <sup>5</sup>	H <sup>6</sup>	H <sup>7</sup>	H <sup>8</sup>	
Exp.	1.01	1.89	6.31	1.77		9.02		9.33				
<i>cis</i> - <b>IIIa</b>	1.21	2.16	6.91	1.78	3.27	8.75	8.46	9.22	8.45	8.38	8.13	0.30
<i>cis</i> - <b>IIIb</b>	2.34	1.83	5.26	2.09	3.04	8.63	8.30	8.93	8.34	8.30	7.95	0.74
<i>trans</i> - <b>IIIa</b>	1.19	2.36	6.84	2.06	3.40	8.79	8.46	9.23	8.46	8.41	8.30	0.34
<i>trans</i> - <b>IIIb</b>	2.51	0.65	6.17	1.94	3.30	8.82	8.39	9.08	8.38	8.39	8.13	0.81

<sup>a</sup> Square root from the average of squares of differences between the calculated and the corresponding experimental chemical shifts

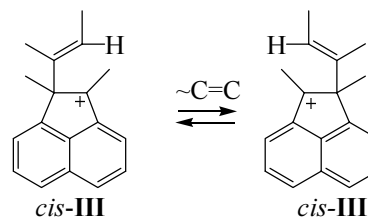
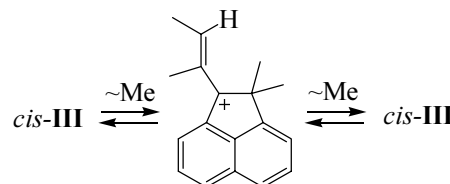
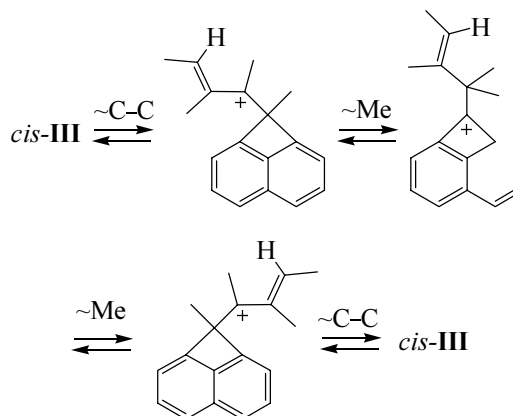
transition *cis*-**IIIb**  $\rightarrow$  **VI** equaled 61.7 kJ mol<sup>-1</sup>). It turned out unexpectedly that for this transition state the oscillation with the negative frequency governing the paths of its transformation led characteristically to displacement of atoms resulting simultaneously in the formation of the C<sup>8</sup>-C<sup>8a</sup> bond, the rupture of the C<sup>6b</sup>-C<sup>8a</sup> bond, and the shortening of the C<sup>6b</sup>-C<sup>7</sup> bond. Consequently the “descent” by procedure IRC from the transition state **B** resulted in formation of a structure **C** with a seven-membered ring which did not correspond to any minimum on PES, and it with no barrier transformed into cation **VI**. Similar conversions are also characteristic of the conformations of cation *trans*-**III** that rearranges into cation **V** (see the figure).

Thus we attained good agreement between the experimental and calculated data; they evidenced that the dimethylvinyl group in cation **III** had the *cis*-configuration. Moreover, these findings show that the formation of a mixture of cations **V** and **VI** in reaction of hydrocarbon **IV** with HSO<sub>3</sub>F [4] is comprehensible if a total *exo*-stereoselectivity would be suggested for the protonation of the hydrocarbon.

The raising of temperature of the solution containing the mixture of carbocations **III**, **V**, and **VI** generated at -130°C caused in the range from -120 to -103°C broadening of signals belonging to the 1-CH<sub>3</sub> group ( $\delta$  1.77) and those from the protons of the aromatic ring of cation *cis*-**III** characteristic of degenerate rearrangements of 1-R-1,2-dimethylacenaphthylenonium ions occurring by 1,2-shift of migrant group R [5, 6, 9] whereas the width of the other signals remained the same or even decreased apparently due to reduced viscosity of the solution. The most probable mechanism of the degenerate rearrangement of cation *cis*-**III** is the 1,2-shift of dimethylvinyl group (Scheme 3). The alternative mechanisms (Schemes 4 and 5) appear improbable: the rate of the 1,2-methyl shift in the 1,1,2-trimethyl-acenaphthylenonium ion is considerably lower than that of the degenerate rearrangement of ion *cis*-**III** (the methyl groups signals

suffer broadening only over 53°C [5]), and the mechanism of the ring contraction–ring expansion does not occur even in the case of the degenerate rearrangement of cation **II** [1] where it is more probable due to the smaller strain of the five-membered ring arising in the first stage as compared to the strain in the four-membered ring presumed in the Scheme 5.

The rate of the degenerate rearrangement of ion *cis*-**III** was estimated from the analysis of the form of the signal from the 1-CH<sub>3</sub> group:  $k$  35 s<sup>-1</sup> at -103°C,  $\Delta G^\ddagger$  35.8 kJ mol<sup>-1</sup>. It is considerably slower than the

**Scheme 3.****Scheme 4.****Scheme 5.**

**Table 2.** Values of free energy of activation for the 1,2-shift of migrant groups R in the degenerate rearrangements of 1-R-1,2-dimethylacenaphthylenonium ions [2]

R	$\Delta G^\ddagger$ , kJ mol <sup>-1</sup>
CH <sub>3</sub>	77 (25°C)
CH <sub>3</sub> CH <sub>2</sub>	71 (25°C)
CH <sub>2</sub> =CHCH <sub>2</sub>	>66 (-50°C)
C <sub>6</sub> H <sub>5</sub>	53.5 (25°C)
<i>cis</i> -C(CH <sub>3</sub> )=CHCH <sub>3</sub>	35.8 (-103°C) <sup>a</sup>

<sup>a</sup> Data of this study.

**Table 3.** Calculated by PBE/3z method barriers to 1,2-shift (kJ mol<sup>-1</sup>)

Cation	Conformation	
	a	b
<i>cis</i> -III	27.5	36.2
<i>trans</i> -III	32.5	43.9

rate of the degenerate rearrangement of ion II ( $\Delta G^\ddagger$  22 kJ mol<sup>-1</sup>) in compliance with the data on the other degenerate rearrangements of 1-R-1,2-dimethylacenaphthylenonium ions as compared with the corresponding 9-R-9,10-dimethylphenanthrenonium ions [2]. It should be noted that the migration ability of the dimethylvinyl group in the 1-R-1,2-dimethylacenaphthylenonium ions is the highest among the hydrocarbon migrant groups (Table 2). The same conclusion we reached in [1] with respect to the degenerate rearrangement of 9-R-9,10-dimethylphenanthrenonium ions.

It is of interest to compare the measured value of the free energy of activation of the degenerate 1,2-shift of the dimethylvinyl group in cation *cis*-III with that calculated by the correlation equation (1) [10] which has been obtained by processing the kinetic data for the 1,2-shifts of various migrant groups in the 1-R-1,2-dimethylacenaphthylenonium ions where the finding for the dimethylvinyl group are lacking. It was presumed in [10] that equation (1) would be valid also for the other migrating groups.

$$\Delta G^\ddagger(-50^\circ\text{C}) = 20.7 + 0.413E_r - 273\text{PA}, \quad (1)$$

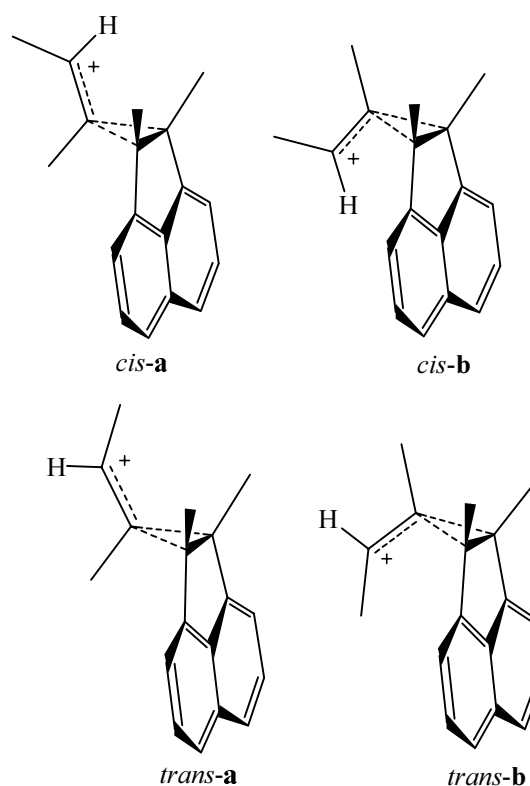
where  $E_r$  is the energy of rupture of the bond migrant-CH<sub>3</sub> (kcal/mol), PA is the proton affinity of the compound migrant-CH<sub>3</sub> (kcal/mol).

We failed to find published data on the energy of the rupture of the C-CH<sub>3</sub> in the molecule of trimethylethene. Assuming that it is close to the corresponding value for the propene molecule (95.1 kcal/mol [11]) and substituting

this value of  $E_r$  and PA 193.3 kcal/mol [12] into the equation (1) we obtain  $\Delta G^\ddagger$  7.2 kcal/mol, fairly close to the experimental result [ $\Delta G^\ddagger(-103^\circ\text{C})$  35.8 kJ mol<sup>-1</sup> = 8.6 kcal/mol].\*

The quantum-chemical calculations of the energy profile for the 1,2-dimethylvinyl shift in ion *cis*-III show that the process proceeds in a single stage, and the calculated value of its energy barrier (27.5 kJ mol<sup>-1</sup>) is close but somewhat underestimated as compared with the experimental finding (35.8 kJ mol<sup>-1</sup>). Analogous situation is observed also for the 1,2-shift of the *cis*-dimethylvinyl group in cation II (18.8 and 22 kJ mol<sup>-1</sup> respectively).\*\*

An interesting point is the effect of the migrating dimethylvinyl group configuration and of the conformation of the ion undergoing the rearrangement on the rate of the degenerate rearrangement. The quantum-chemical calculations (Table 3) show that the migration ability of the *cis*-dimethylvinyl group is higher than that of the *trans*-dimethylvinyl group, and both the migrants in the cations of "a" conformation rearrange easier than in cations of "b" conformations. A similar conformational effect for



\* The free energy of activation of the degenerate rearrangements of carbocations usually does not depend on the temperature.

\*\* According to calculations performed in this study by PBE/3z method.

cations with the phenanthrenonium skeleton was stated in [13] and was ascribed to the negative effect caused by the interaction between the  $\pi$ -orbital of the  $\beta$ -carbon in the vinyl group and  $\pi$ -orbitals of the aromatic rings in the activated complexes of the “b” type. The view of the activated complexes in the degenerate rearrangement of cations *cis*-**III** and *trans*-**III** is shown below.

The data of Table 3 and of the figure show further the effect of the conformational transformations of the rate of the degenerate rearrangement. Inasmuch as the relative stability of conformer *cis*-**IIIa** is higher and the barrier to the one-stage degenerate rearrangement for this conformer is lower than that for “b” conformer in this case the conformational effects are not revealed, and the rearrangement occurs along the one-stage *cis*-**IIIa**  $\rightleftharpoons$  *cis*-**IIIa**. But for cation *trans*-**III** conformer “b” is more stable, and its barrier to the one-stage degenerate rearrangement is higher (43.9 kJ mol<sup>-1</sup>) than the barrier to the conformational transition *trans*-**IIIb**  $\rightleftharpoons$  *trans*-**IIIa** (38.9 kJ mol<sup>-1</sup>) (see the figure). Taking the above into account it is possible to conclude that the degenerate rearrangement of cation *trans*-**III** occurs in three stages: *trans*-**IIIb**  $\rightleftharpoons$  *trans*-**IIIa**  $\rightleftharpoons$  *trans*-**IIIa**  $\rightleftharpoons$  *trans*-**IIIb**; therewith the barrier to the degenerate rearrangement equals 39.7 (7.2 + 32.5) kJ mol<sup>-1</sup>.

The quantum-chemical calculations suggest that the configuration of the dimethylvinyl group in the 1-dimethylvinyl-1,2-dimethylacenaphthylenonium ions significantly affects also their nondegenerate rearrangements: Cation *cis*-**III** transforms only into cation **VI** (the activation barrier for this rearrangement is by 6.7 kJ mol<sup>-1</sup> lower than the barrier for rearrangement into cation **V**), and cation *trans*-**III** rearranges into cation **V** (here  $\Delta\Delta E = 14.6$  kJ mol<sup>-1</sup>), and both processes occur in one stage.

## EXPERIMENTAL

The <sup>1</sup>H NMR spectra of carbocations were registered on a spectrometer Bruker AM 400 using the residual protons of CD<sub>2</sub>Cl<sub>2</sub> as internal reference ( $\delta$  5.33 ppm). The temperature in the probe of the spectrometer at -130°C was calibrated by the melting point of the chemically pure sample of n-pentane, over -90°C was used a standard methanol sample. For intermediate temperatures the linear interpolation was employed. The generation of carbocations was performed by interaction of solutions of olefin **IV** [3, 4] in CD<sub>2</sub>Cl<sub>2</sub> and HSO<sub>3</sub>F in SO<sub>2</sub>ClF at -130°C by procedure described in [1]. Before use HSO<sub>3</sub>F was twice distilled (bp 158–161°C), SO<sub>2</sub>ClF

[14] was dried by passing its vapor through concn. H<sub>2</sub>SO<sub>4</sub>, and CD<sub>2</sub>Cl<sub>2</sub> was dried over molecular sieves 4A.

Quantum-chemical calculations of the geometry of carbocations and their NMR chemical shifts were performed by DFT method in the PBE approximation [15] using routine “Priroda” [16] {basis 3z, (11s6p2d)/[6s3p2d] for C and (5s1p)/[3s1p] for H}. The calculation of exchange NMR spectra was carried out with the use of MEX software [17] incorporated into xsim package [see ftp://nmr.nioch.nsc.ru/pub/nmr/].

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