

Dedicated to the memory of Full Member of the Academy of Sciences of the USSR
N.N. Vorozhtsov on the 100th anniversary of his birth

Pendular Rearrangement of Epimeric 3b,4,4a,5-Tetramethyl-3b,4,4a,5-tetrahydro-4H-cyclopropa[a]phenalen-5-yl Cations

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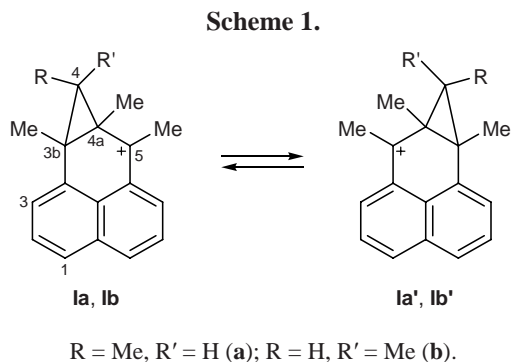
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Abstract—The kinetics of degenerate pendular rearrangement of 3b,exo-4,4a,5-tetramethyl-3b,4,4a,5-tetrahydro-4H-cyclopropa[a]phenalen-5-yl cation and its *endo* epimer, generated under conditions ensuring their long life, were studied by dynamic NMR spectroscopy. The rearrangement mechanism is discussed with account taken of the results of quantum-chemical calculations and published data for related rearrangements.

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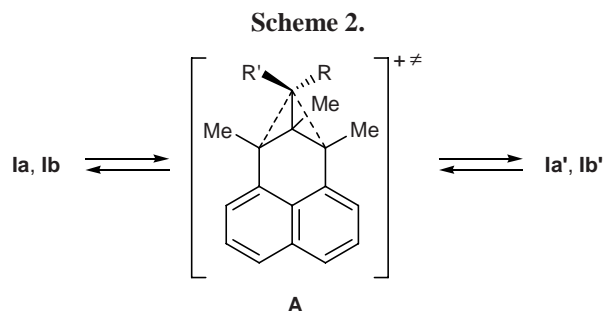
Using ^1H NMR spectroscopy we previously [1] revealed degenerate rearrangement of 3b,exo-4,4a,5-tetramethyl-3b,4,4a,5-tetrahydro-4H-cyclopropa[a]phenalen-5-yl cation (**1a**) and its *endo* epimer **1b** which were generated under conditions ensuring their long life (Scheme 1).

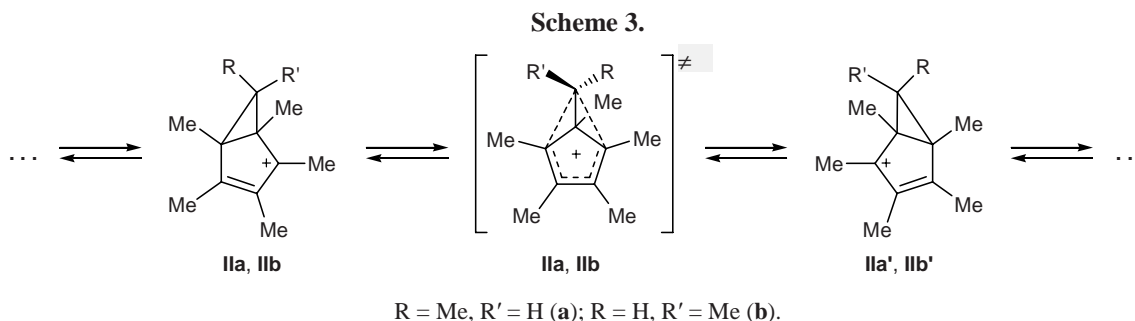


Specificity of this rearrangement is that the bond between the C^4 and C^{4a} atoms is retained, while the C^4 atom appears to be linked to C^5 (cationic center), so that the three-membered ring is transferred to another side of the six-membered ring. Here, the groups attached to C^4 do not change their position, i.e., there is no interconversion of cations **1a** and **1b**. Reversible migrations of the $\text{C}^{3b}\text{--C}^4$ bond resemble pendular motion; therefore, the observed rearrangement may be referred to as *pendular*.

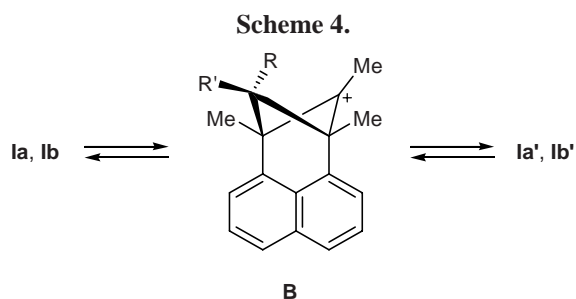
The goal of the present work was to study the kinetics and mechanism of the above degenerate rearrangement. Its kinetics were studied by dynamic NMR spectroscopy, and the results are collected in Table 1. As might be expected (cf. the data for other degenerate rearrangements of long-lived carbocations involving migrations of hydrocarbon groups [2]), the rate of the rearrangement of cations **1a** and **1b** almost does not depend on the acidity of the medium (Table 2).

Scheme 2 shows a one-step mechanism of the rearrangement which seems *a priori* to be the most probable. It is analogous to the mechanism of related circumambulatory rearrangement of bicyclo[3.1.0]hexenyl cations like **II** (Scheme 3) [3–6]. Its specific feature is inversion of configuration of that carbon atom in the three-membered ring which forms a bond with the cationic center. According to Woodward–Hoffmann [7], such mechanism pertains to thermally allowed 1,4-C–C bond shifts.

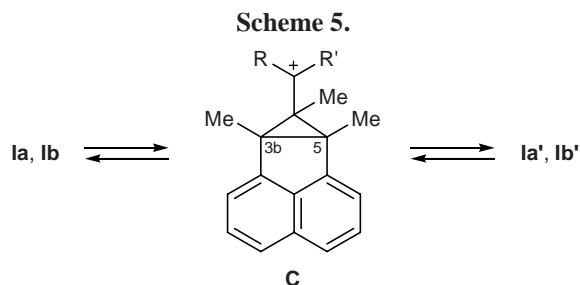




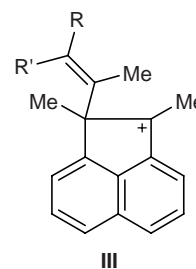
A two-step mechanism involving successive 1,2-C–C shifts with formation of cyclobutyl-like cationic intermediates **B** (Scheme 4) was considered in [8]; it was proposed for some long-lived cyclopropylcarbinyl cations. However, this mechanism is not confirmed by the results of quantum-chemical calculations. First, structure **B** is not an intermediate but a high-energy transition state [9] (Fig. 1). Second, it implies that the rate of degenerate rearrangement of cation **Ib** would be higher than the rate of rearrangement of cation **Ia**. According to the calculations [9], **Ia** is more stable than **Ib** (Fig. 1), and transition state **B** corresponding to the rearrangement of **Ib** has lower energy than that for **Ia** ($\Delta E = 3.4$ kJ/mol).



Another two-step mechanism involving cyclopropylcarbinyl cation **C** as intermediate (Scheme 5) also seems to be improbable. As follows from the calculations, coercive approach of the C^{3b} and C⁵ atoms to each other in cations **Ia** and **Ib** leads to transition states like **D** with loosening of the C^{3b}–C^{4a} bond (cf. [9]) and then to ions **III** with *cis*- and *trans*-dimethylvinyl



groups, respectively (Scheme 6) rather than to intermediates like **C**. Moreover, according to our recent data [9], structures like **C** are not intermediates but transition states for 1,2-vinyl shift in degenerate rearrangements of ions **III**.



Degenerate rearrangements of ions **Ia** and **Ib** are unlikely to follow Scheme 6. The calculated energy barriers to the transformations of **Ia** and **Ib** into type

Table 1. Kinetic parameters of degenerate rearrangements of cations **Ia** and **Ib** in HSO₃F–CD₂Cl₂ (2:1, by volume)^a

Cation	E_a , kJ/mol	log A	ΔH^\ddagger , kJ/mol	ΔS^\ddagger , J mol ⁻¹ K ⁻¹
Ia	43.0±1.4	11.0±0.3	40.7±1.4	-42.9±5.5
Ib	52.3±2.1	11.0±0.4	49.7±2.1	-42.2±7.3

^a Standard deviations are given with account taken of the Student coefficient for a confidence probability of 0.99.

Table 2. Gibbs energies of activation for degenerate rearrangements of cations **Ia** and **Ib** in acid media at 25°C

Cation	Medium (volume ratio)	ΔG^\ddagger , kJ/mol
Ia	HSO ₃ F–CD ₂ Cl ₂ (2:1)	53
	CF ₃ SO ₃ H–CDCl ₃ (4:1)	54
Ib	HSO ₃ F–CD ₂ Cl ₂ (4:1)	63
	HSO ₃ F–CD ₂ Cl ₂ (2:1)	62
	CF ₃ SO ₃ H–CD ₂ Cl ₂ (4:1)	64
	CF ₃ SO ₃ H–CDCl ₃ (4:1)	64
	CF ₃ SO ₃ H–CDCl ₃ (1:2)	64

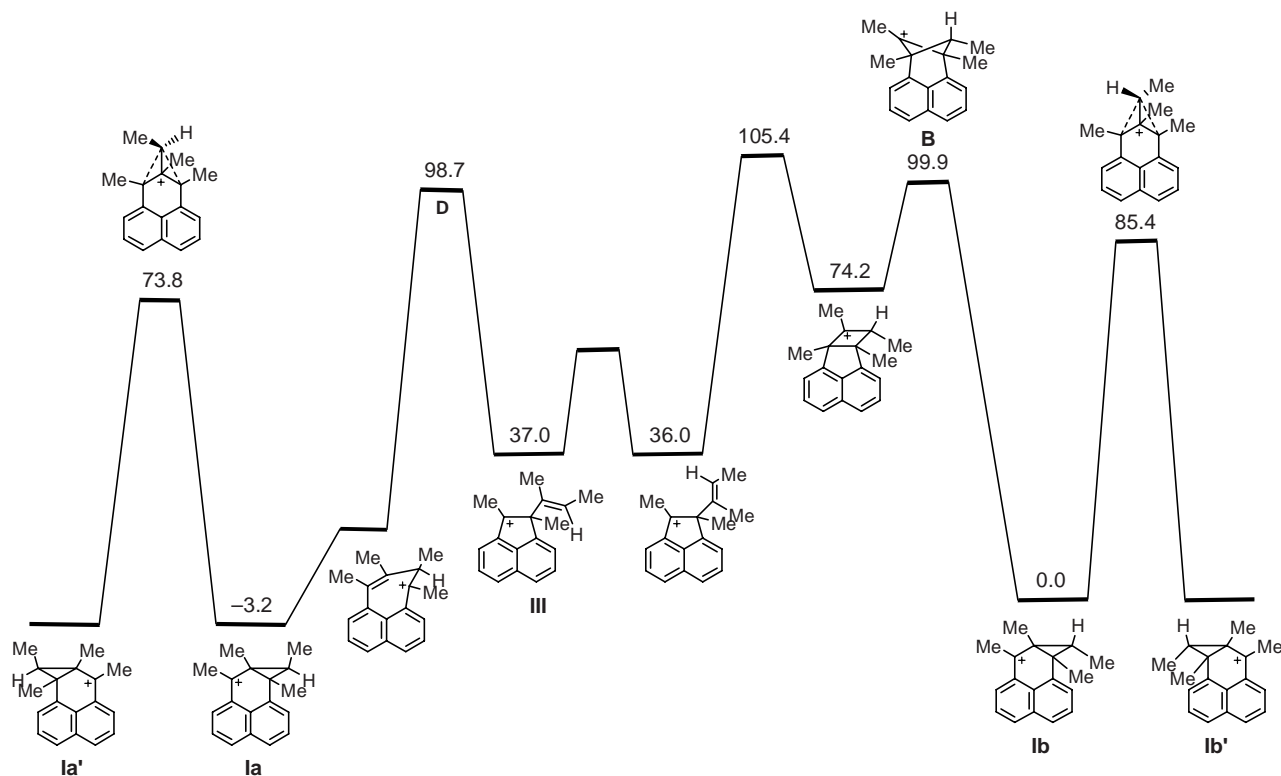
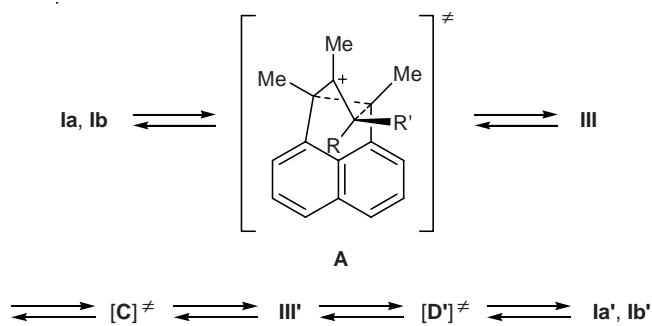


Fig. 1. Calculated energy profile for carbocationic rearrangements; relative energies (kJ/mol) are given.

III cations (101.9 and 119.7 kJ/mol, respectively [9]) are much higher than those found experimentally (Table 1).

the mechanism of circumambulatory rearrangement of ions **IIa** and **IIb** (Scheme 3). On the other hand, the three-membered ring in **Ia** and **Ib** is fused to six-membered ring rather than five-membered as in **IIa** and **IIb**; the six-membered ring in the former is in turn *peri*-fused to aromatic naphthalene fragment, which gives rise to some specificity in the rearrangement of **Ia** and **Ib**. Unlike circumambulatory rearrangement which involves in succession both side bonds of the three-membered ring (and the latter migrates in both directions in a circular mode), only one of the two

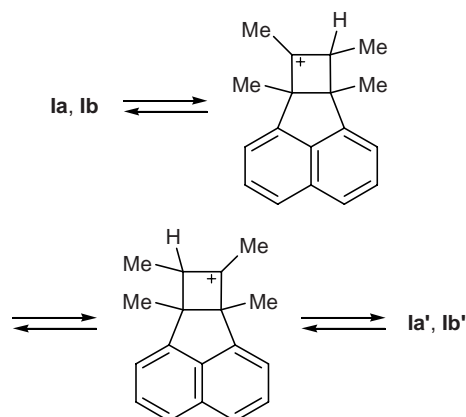
Scheme 6.

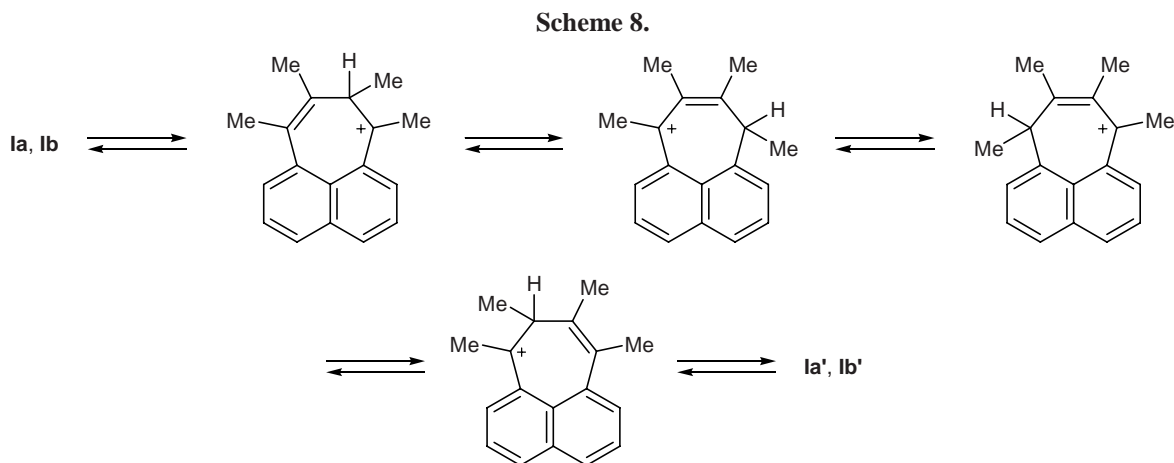


The mechanisms shown in Schemes 7 and 8 should be ruled out for the following reason. Had they been operative, signals not only from 3b-Me and 5-Me but also from 4-Me and 4a-Me groups in the ^1H NMR spectra would be averaged (cf. [1]); however, this is not observed experimentally.

Thus the mechanism shown in Scheme 2 should be accepted for the pendular degenerate rearrangement of cations **Ia** and **Ib**. As we already noted, it is similar to

Scheme 7.





nonequivalent side bonds participates in the pendular rearrangement, and circular migration of the three-membered ring is excluded. One more difference between these rearrangement is that the corresponding transition states have essentially different structures (according to quantum-chemical calculations; Table 3). The transition state in the pendular rearrangement is similar to structure **B**, while that found for the circumambulatory rearrangement is closer to “opened” methyl(pentamethylcyclopentadienyl)methyl cation (Fig. 2).

Quantum-chemical calculations gave energy barriers of 77.0 and 85.4 kJ/mol for pendular degenerate rearrangements of epimeric cations **Ia** and **Ib**, respectively. These values exceed the experimental barriers, but the difference between the barriers for **Ia** and **Ib** is reproduced well. Presumably, the lower rate of degenerate rearrangement of cation **Ib** compared to **Ia** results from unfavorable spatial interaction between the *endo*-methyl group and skeletal atoms in the transition state (cf. [4]).

According to Brouwer and Hogeveen [10], the described pendular degenerate rearrangement, as well as many other rearrangements of carbocations, is a particular case of intramolecular electrophilic substitution (S_Ei reaction).

EXPERIMENTAL

Carbocations were generated using commercial trifluoromethanesulfonic acid (Aldrich), doubly distilled fluorosulfonic acid (bp 158–161°C), and $CDCl_3$ and CD_2Cl_2 dried over 4-Å molecular sieves. Cations **Ia** and **Ib** were generated by adding a solution of 6b,7,8,8a-tetramethyl-6b,8a-dihydrocyclobuta[*a*]acenaphthylene [1] in $CDCl_3$ or CD_2Cl_2 to CF_3SO_3H or HSO_3F under stirring at 0°C.

The temperature of NMR probes (Bruker AM-400 and DRX-500) was calibrated using a standard sample of methanol (–50 to 25°C) and naphthalene (mp 80°C); interpolation was performed for intermediate temperatures.

The rate constants for pendular rearrangements of cations **Ia** and **Ib** were determined by comparing the

Table 3. Distances (d , Å) between carbon atoms in the transition states for rearrangements of cations **I** and **II**^a

Distance	Ia	Ib	IIa	IIb
$C^{3b(5)}-C^4$	1.739	1.675	2.169	2.282
$C^{3b(5)}-C^{4a}$	1.453	1.464	1.500	1.507
C^4-C^{4a}	1.680	1.755	1.497	1.492

^a Atom numbering in the three-membered ring in ions **I** and **II** is assumed to be the same.

Table 4. Rate constants (s^{-1}) of degenerate rearrangements of cations **Ia** and **Ib** in $HSO_3F-CD_2Cl_2$ (2:1, by volume)

Temperature, °C	Ia	Ib
–43	4 ^a ; 4 ^b	–
–33	13 ^a ; 12 ^b	–
–23	43 ^a ; 41 ^b	–
–13	100 ^a ; 110 ^b	2 ^c
–3	300 ^a	5.5 ^a ; 5.5 ^b ; 5 ^c
7	800 ^a	15 ^a ; 13 ^b ; 15 ^c
17	1700 ^a ; 1700 ^b	40 ^a ; 34 ^b ; 37 ^c
27	3000 ^a ; 3000 ^b	90 ^a ; 78 ^b ; 95 ^c
37	–	180 ^a ; 200 ^b ; 220 ^c
47	–	500 ^a ; 500 ^c

^a Calculated from signals of aromatic protons.

^b Calculated from signals of protons in the 3b-CH₃ and 5-CH₃ groups.

^c Calculated from the C² and C⁷ signals.

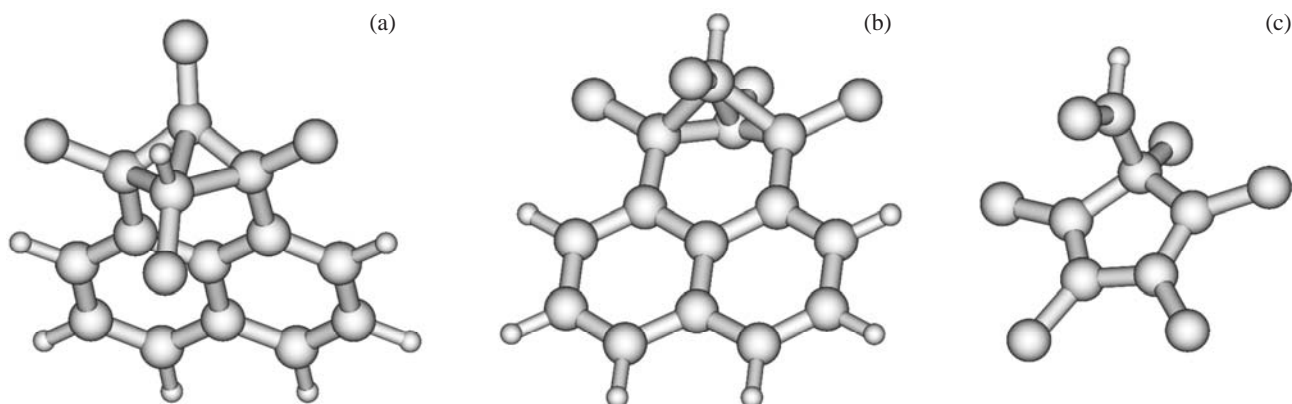


Fig. 2. Calculated structures of transition states for (a, b) pendular rearrangement of cation **IIb** (two projections) and (c) circumambulatory rearrangement of cation **IIb**. Methyl hydrogen atoms are not shown. The structures of transition states for the degenerate rearrangements of cations **Ia** and **IIa** are similar.

experimental NMR spectra with exchange spectra calculated by MEX and MEXICO programs [11]. The kinetic parameters (Table 1) were determined from the temperature dependence of the rate constants (Table 4) using the Arrhenius and Eyring equations.

Quantum-chemical calculations of the geometric parameters and energies of cations were performed by the DFT method {PBE potential [12]; 3ζ basis set, (11s6p2d)/[6s3p2d] for carbon atoms and (5s1p)/[3s1p] for hydrogen atoms} using Priroda software [13].

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