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Carbocationic Cyclizations: IX.* Rearrangement of Long-Lived 4-(2-Biphenylyl)-1,2,3,4-tetramethylcyclobutenyl Cation into *trans*- and *cis*-4,5,6,6-Tetramethyl-4,5,6-trihydrocyclopenta[*j*,*k*]phenanthren-5-yl Cations

V. A. Bushmelev, A. M. Genaev, S. A. Osadchii, M. M. Shakirov, and V. G. Shubin

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia
e-mail: bushmelev@nioch.nsc.ru

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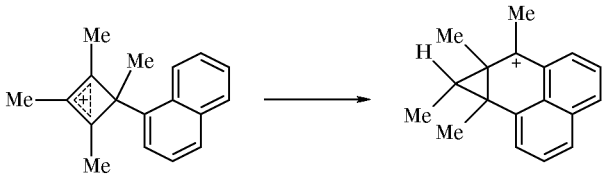
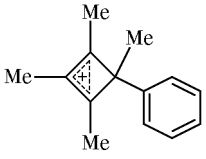
Abstract—According to the ^{1}H and ^{13}C NMR data, long-lived 4-(2-biphenylyl)-1,2,3,4-tetramethylcyclobutenyl cation generated by protonation of 3-(2-biphenylyl)-1,2,3-trimethyl-4-methylenecyclobutene in superacids undergoes cyclization which launches further rearrangements finally leading to formation of a mixture of *trans*- and *cis*-4,5,6,6-tetramethyl-4,5,6-trihydrocyclopenta[*j*,*k*]phenanthren-5-yl cations.

Carbocationic cyclizations (intramolecular alkylation) with participation of long-lived carbocations containing aromatic fragments lie at the interface between the chemistry of carbocations and aromatic compounds. Investigation of these reactions by modern experimental and theoretical methods makes it possible to get an insight into their mechanism and and disclose their synthetic potential.

In the preceding communication of this series [1] we have reported that 4-(1-naphthyl)-1,2,3,4-tetramethylcyclobutenyl cation (**I**) generated in superacidic medium undergoes cyclization involving the unsubstituted α-carbon atom. This reaction gives rise to subsequent carbocationic rearrangements which eventually led to formation of phenalene cation **II**. Unlike cation **I**, 4-phenyl-1,2,3,4-tetramethylcyclobutenyl cation (**III**) is not prone to cyclization [2].

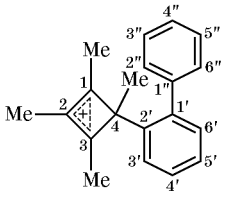


I **II**

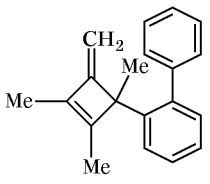


III

With the goal of extending the series of related carbocations through variation of aromatic fragments therein, as subject for study we selected 4-(2-biphenylyl)-1,2,3,4-tetramethylcyclobutenyl cation (**IV**). We anticipated that more favorable steric factors, as compared to **III** (specifically, the possibility for formation of a six- rather than four-membered ring via attack by electrophilic carbocationic center on the aromatic fragment), should make the cyclization of **IV** possible. However, one cannot rule out *a priori* that the above factor could appear so strong that carbocation **IV** could not be generated with a sufficient lifetime because of high rate of its cyclization. It should be noted that the cyclization of **I**, which



IV



V

* For communication VIII, see [1].

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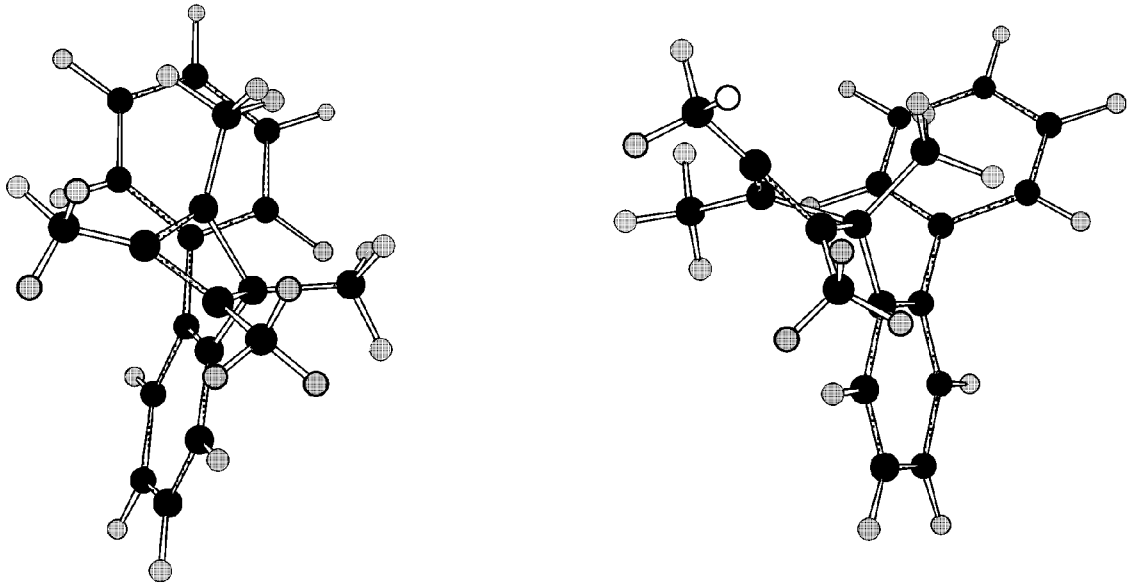


IVA **IVB**

Fig. 1. Conformations of cation **IV**, calculated by the MINDO/3 method.

(according to Baldwin [3]) is classed with "disfavored 5-*endo-trig*," is nevertheless characterized by a high rate even at low temperature ($k^{-20°C} = 7 \times 10^{-4}$ s^{-1}, $\Delta G^{\neq} = 77$ kJ/mol) [1], whereas the cyclization of **IV** is referred to as "favored 6-*endo-trig*" process.

Thus the present study was aimed at elucidating the possibility for generation of long-lived cation **IV** and (provided that the generation is successful) examining its rearrangements. Analysis of the NMR spectra of solutions of 3-(2-biphenylyl)-1,2,3-trimethyl-4-methylenecyclobutene (**V**) in the superacidic system HSO_3F/SbF_5–SO_2ClF–CD_2Cl_2 (1 : 4 : 1, by volume), prepared at low temperatures, showed that generation of long-lived cation **IV** was successful at –110 to –120°C; ^{1}H NMR spectrum (–121°C, 200.13 MHz), δ, ppm: 1.21 br.s (3H, 3-CH_3), 1.73 s (3H, 4-CH_3), 2.19 s (3H, 2-CH_3), 2.57 br.s (3H, 1-CH_3), 7.0–8.8 m (9H, H_{arom}). It is characteristic that the methyl groups in positions *1* and *3* of cation **IV** are nonequivalent. The ^{13}C NMR spectrum (–112°C, 50.323 MHz) contained the following signals, δ_C, ppm: 10.5 (2-CH_3); 11.5 (broadened signal from two methyl carbon nuclei, 1- and 3-CH_3); 19.5 (4-CH_3); 73.0 (C^4); 126–134, 138.2, 140.8, and 142.1 (C_{arom}, biphenylyl fragment); ~165.0 (strongly broadened and therefore difficult to identify, C^1 and C^3); 183.2 (C^2). The signals were assigned with account taken of known spectral data for 4-R-substituted 1,2,3,4-tetramethylcyclobutenyl cations, where R = 1-naphthyl [1], Ph [2], $PhCH_2$ [4], and CH_3 [2].

A considerable difference in the chemical shifts of the 1-CH_3 and 3-CH_3 protons (Δδ 1.36 ppm) in the ^{1}H NMR spectrum of cation **IV** arises from restricted rotation about the C^4–$C^{2'}$ bond. As a result, protons of the 1-CH_3 group suffer stronger deshielding effect of the aromatic fragment due to its magnetic anisotropy. Figure 1 shows the structure of cation **IV** according to the MINDO/3 calculations.** Conformer **IVA** differs from less stable conformer **B** by morphology of the four-membered ring: in particular, the C^2 atom in **IVA** appears spatially close to the phenylene fragment. One methyl group in **IVA** (1- or 3-CH_3) is located in the area of shielding by the phenyl group which is turned through an angle of 90° relative to the *o*-phenylene moiety, whereas the other methyl group resides in the area of deshielding by the *o*-phenylene fragment. Calculation of the chemical shifts of the 1-CH_3 and 3-CH_3 protons in conformer **IVA** by the IGLO method [6] using the DZ basis set gave a Δδ value of 1.10 ppm which approaches that found experimentally. It would be attractive to anticipate that, apart from magnetic anisotropy of the aromatic fragment, some contribution to the difference in the chemical shifts of the 1-CH_3 and 3-CH_3 protons is given by their diastereotopy arising from appearance of a chiral center as a result of second protonation at the $C^{2'}$ atom. However, there were no reasons for

** Among semiempirical methods, the MINDO/3 approximation is known [5] to reproduce the energy parameters of carbocations most properly.

such assumption: according to the ^{13}C NMR data, no dication was formed (cf. ^{13}C NMR data for arenonium ions in [7]).

On raising the solution temperature to –103°C the signals from C^1, C^3, 1-CH_3, and 3-CH_3 in the ^{13}C NMR spectrum become narrower. Simultaneously, the ^1H signals from the 1-CH_3 and 3-CH_3 groups initially broaden (at –120 to –100°C) and then merge together (–103°C) to give one signal at δ 1.9 ppm, which becomes narrower on further raising the temperature. Obviously, this pattern is explained by resumption of free rotation of the biphenylyl fragment about the $C^4-C^{2'}$ bond. Estimation of the barrier to rotation by the dynamic NMR procedure gave a $\Delta G^{\neq}$ value of 31 kJ/mol (–121°C). The barrier calculated by the MINDO/3 method is 37 kJ/mol (Fig. 2). Analogous ^1H and ^{13}C NMR spectra were obtained for solutions of compound **V** in the system HSO_3F–SO_2ClF–CD_2Cl_2 (1:4:1, by volume).

It should be noted that rotation about the $C^4-C^{2'}$ bond in cation **IV** is not accompanied by overlap of van der Waals spheres of atoms which are not linked through covalent bonds. This is consistent with the very low energy barrier to rotation about analogous C–Ar bond in neutral compound **V** (precursor of cation **IV**; Fig. 2). Both species, **IV** and **V**, are characterized by similar geometric parameters. Therefore, we presume that the main factor responsible for restricted rotation in the cation is donor–acceptor interaction between its biphenylyl and electron-deficient cyclobutane fragments. Comparison of the heats of formation of conformers **IVA** and **IVB** (Fig. 2) shows that the above donor–acceptor interaction is stronger in the former where, as we already noted, the C^2 atom appears in the vicinity of the phenylene group. This fact, as well as the other geometric parameters of structure **IVA**, led us to conclude that the electron-donor component is just the *o*-phenylene moiety of the biphenyl fragment.

The existence of donor–acceptor interaction in cation **IV** is also supported by its ^{13}C NMR spectrum. It is known that variation of the angle between the $C^2C^1C^3$ and $C^4C^1C^3$ planes in cyclobutenyl-like carbocations requires no large energy to be spent but leads to considerable change in the chemical shifts of the C^1 and C^3 atoms. As the above angle decreases, the C^1 and C^3 signals shift upfield, the magnitude of the shift reaching 2.5 ppm per degree [8]. Comparison of the ^{13}C NMR parameters of cation **IV** (δ_{C^1,C^3} = 165 ppm) and 1,2,3,4,4-pentamethylcyclobutenyl cation (δ_{C^1,C^3} = 183.7 ppm), which lacks such donor–acceptor interaction, suggests that the structure of **IV** is actually characterized by increased puckering of the four-membered ring. It is reasonable to believe that this puckering results from donor–acceptor interaction in cation **IV**.

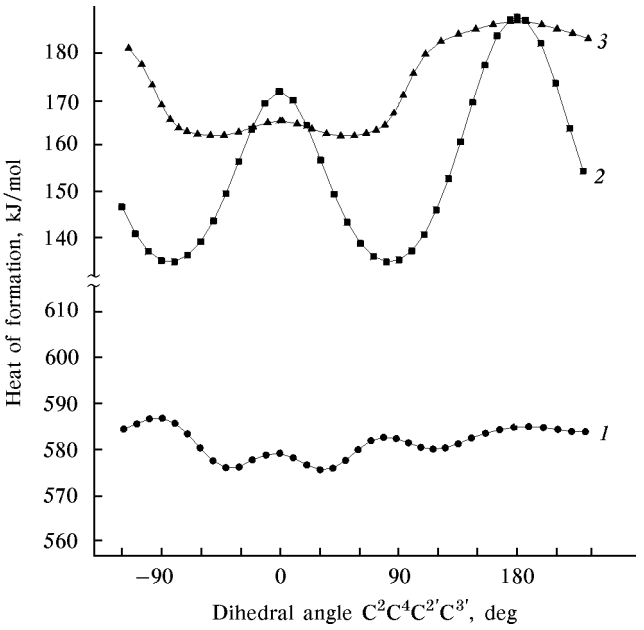


Fig. 2. Barriers to rotation about the $C^4-C^{2'}$ bond in (*1*) olefin **V**, (*2*) conformer **IVA**, and (*3*) conformer **IVB**, calculated by the MINDO/3 method.

According to the ^1H and ^{13}C NMR data, gradual raising the temperature of a solution containing cation **IV** in HSO_3F–SO_2ClF–CD_2Cl_2 above –100°C leads to irreversible isomerization into a mixture of *trans*- and *cis*-4,5,6,6-tetramethyl-4,5,6-trihydrocyclopenta[*j,k*]-phenanthren-5-yl cations **VIa** and **VIb**, respectively, at a ratio of 1:2 (–35°C). During this process, three unidentified species successively appear and disappear. We failed to identify these species, for it was necessary to assign all signals belonging thereto from a complex set of the observed signals which are overlapped in many regions.

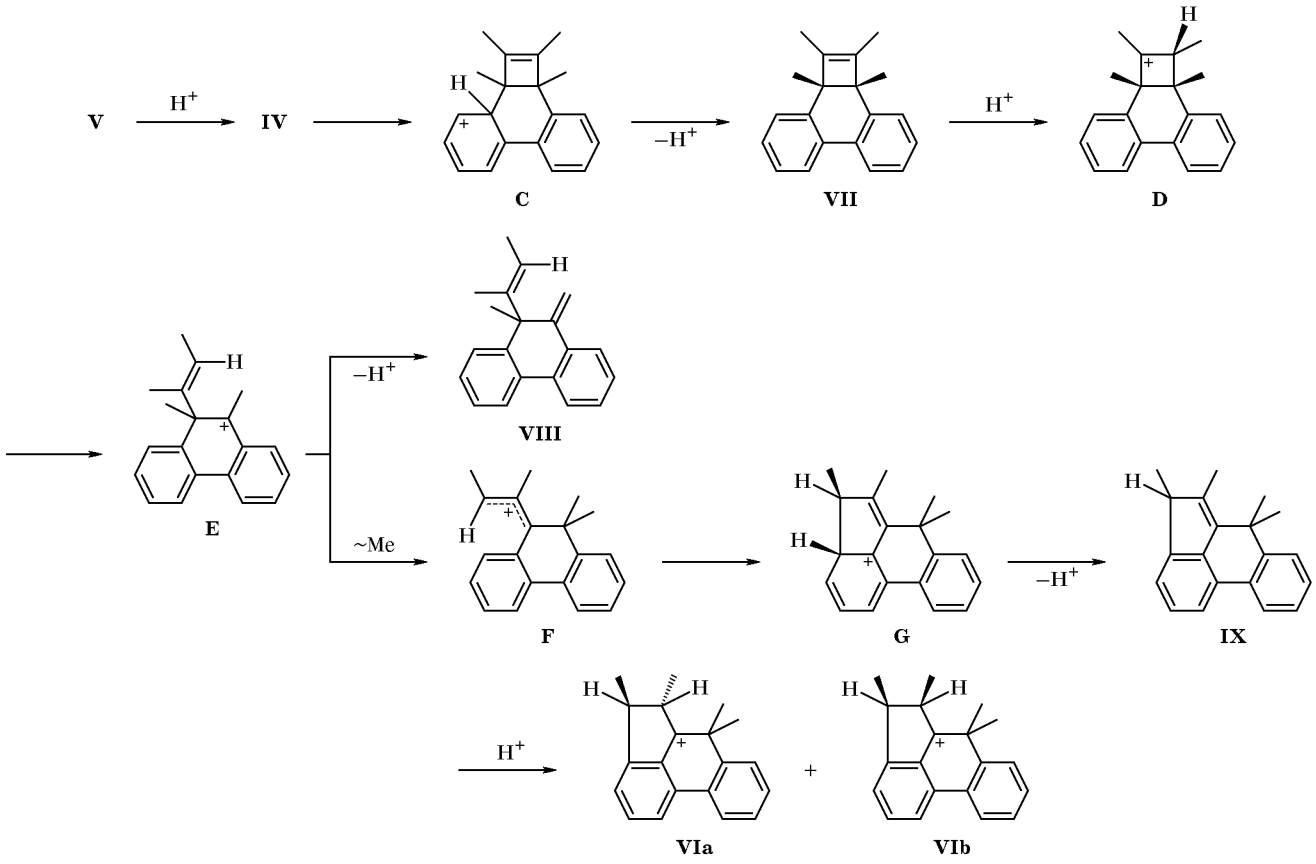
A mixture of cations **VIa** and **VIb** was also obtained from the product of cyclization of cation **IV**, 1,2,2a,10b-tetramethyl-2a,10b-dihydrocyclobuta[*l*]-phenanthrene (**VII**), when its solution in CD_2Cl_2 (1 volume) was added to the acid system HSO_3–SO_2ClF (1:4, by volume) at –130°C and the resulting mixture was allowed to warm up to –30°C or when powdered compound **VII** was dissolved in HSO_3F at –85°C and the solution was allowed to warm up to –50 to –30°C. In the first case, we succeeded in detecting intermediate species whose spectral parameters coincided with those of unidentified species formed from cation **IV**. These findings suggest that

hydrocarbon **VII** (which is obtained from diene **V** by the action of 85% phosphoric acid) is formed as intermediate in the rearrangement of **IV** into a mixture of cations **VIa** and **VIb**. Addition of a solution of **VII** (1 volume) to a mixture of CF_3SO_3H with $CDCl_3$ (2:1, by volume) at room temperature afforded only *trans* isomer **VIa**. Probably, these conditions correspond to equilibrium between isomeric cations **VIa** and **VIb**, where the former (*trans*) predominates as more thermodynamically stable isomer.

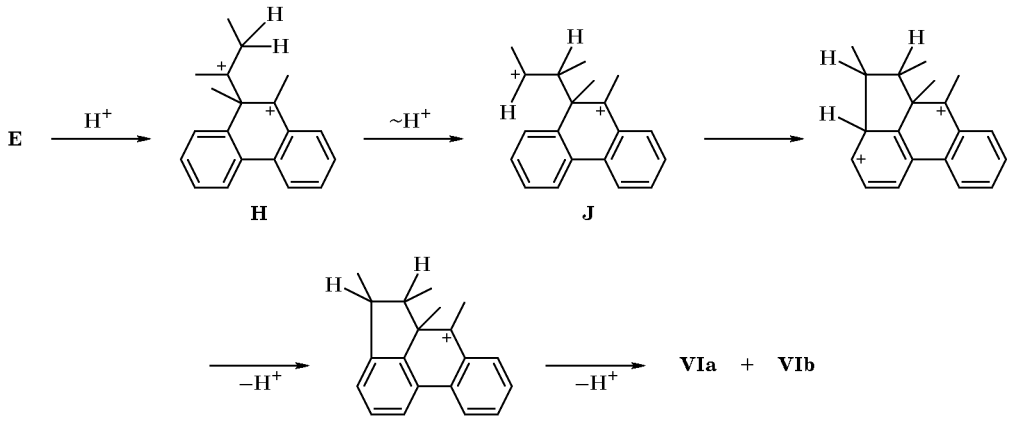
A solution of **VII** in HSO_3F–SO_2ClF–CH_2Cl_2 (1:4:1), prepared at –100°C, was neutralized by adding it in a dropwise manner to a mixture of ether, sodium carbonate, triethylamine, and a small amount of methanol, cooled to –100°C. As a result, we isolated only 9-methyl-9-(*cis*-1-methyl-1-propenyl)-10-methylene-9,10-dihydrophenanthrene (**VIII**) and 4,5,6,6-tetramethyl-4,6-dihydrocyclopenta[*j*,*k*]phenanthrene (**IX**). The formation of these products suggests that one more intermediate in the transformation of **IV** into **VI** is 9-(*cis*-1-methyl-1-propenyl)-9,10-dimethylphenanthrenium ion **E**. The fact that olefin **VIII** was formed as a single isomer with *cis* arrangement of the methyl groups indicates stereoselective character of protonation of tetracyclic olefin **VII**: proton adds exclusively from the *exo* side, for only in this case allowed disrotatory opening of the four-membered ring in protonated compound **VII** could afford cation **E**. An analogous pattern in the protonation of olefins containing a cyclobutene fragment was observed by us previously [1, 4]. As expected, quenching of a solution of **VII** in CF_3SO_3H–$CDCl_3$ (1:1, by volume), prepared at 20°C, gave only compound **IX**. In keeping with the above stated, Scheme 1 shows a plausible mechanism of the isomerization of cation **IV** into phenanthrenium ions **VIa** and **VIb** (hereinafter, each chiral structure corresponds in fact to an equimolar mixture of enantiomers).

The presence of geminal methyl groups in the final rearrangement products (cations **VIa** and **VIb**) implies 1,2-migration of methyl group in intermediate phenanthrenium ion **E** (cf. [7]) and subsequent transformation of allylic cation **F** (which is more stable than **E** by 23 kJ/mol, according to the MINDO/3 calculations) through cation **G** and compound **IX** to cations **VIa** and **VIb** (cf. [9]). The absence of a product which might be formed from cation **F** among those obtained by neutralization of a solution of **V** in HSO_3F–

Scheme 1.



Scheme 2.



$SO_2ClF–SH_2Cl_2$, prepared at –100°C, may be explained on the assumption that the rate of the 1,2-CH_3 shift in cation **E** is lower than the rate of cyclization of **F**. The reason for the much lower rate of 1,2-CH_3 shift in **E**, as compared with analogous process in 9,9,10-trimethylphenanthrenium cation [7], may be homoallyl interaction in the former. Obviously, the rearrangement of **IV** gives a mixture of isomeric cations **VIa** and **VIb** because of the lack of stereoselectivity in the protonation of olefinic intermediate **IX**. According to the ^1H and ^{13}C NMR spectral data, a mixture of cations **VIa** and **VIb** was also formed by rearrangement of cation **IV** in the acid system $HSO_3F–SbF_5–SO_2ClF–CD_2Cl_2$. Apart from signals belonging to **VIa** and **VIb**, the NMR spectra contained signals of an unknown species, other than those detected in the acid system containing no SbF_5. The relative concentration of this species remained constant on raising the temperature up to –35°C. Taking into account the higher acidity of the SbF_5-containing system, as compared to $HSO_3F–SO_2ClF–CD_2Cl_2$, we presume that in this case the rearrangement of **IV** into phenathrenium ions **VIa** and **VIb** involves dicationic intermediates generated from ion **E**. Here, we cannot rule out direct formation of dication **J** from cation **E** via anti-Markownikoff proton addition. This pathway is favored by the lower energy of Coulomb interaction between positive charges in the resulting dication (Scheme 2).

The formation of hydrocarbon **VII** as a result of acid-catalyzed cyclization of diene **V** by the action of 85% phosphoric acid may be interpreted in terms of insufficient acidity of the medium, which does not ensure protonation of **VII** at the endocyclic cyclobutene double bond to an extent required for successful further transformations. The rate of cyclization of cation **IV** at about –100°C is considerably higher than the rate of cyclization of cation **I**, though the nucleophilicity of carbon atom in the biphenylyl fragment of **IV** (which is subjected to electrophilic attack by the carbocationic center at the stage of cyclization) should be much lower than the nucleophilicity of the corresponding carbon atom in the α-naphthyl group in cation **I** (cf. the basicities of biphenyl and naphthalene [10]). The most probable reason is favorable steric factors, in keeping with the Baldwin rules [3].

Thus, unlike previously examined carbocations having allyl [11, 12], benzyl [4], and α-naphthyl groups [1], whose rearrangements afforded finally carbocations with a cyclopropylcarbinyl fragment, the isomerization of cation **IV** gives rise to tetracyclic cations **VI** of the phenanthrene series. The rearrangement of **IV** into **VIa** and **VIb** attracts certain interest from the synthetic viewpoint as an example of transformation of a $C_4–C_6–C_6$ nonfused tricyclic system into a $C_5–C_6–C_6–C_6$ fused tetracyclic system.

EXPERIMENTAL***

The ^1H NMR spectra were recorded on Bruker AC-200, AM-400, and WP-200SY spectrometers. The ^{13}C NMR spectra were obtained on a Bruker AC-200 instrument (50.323 MHz) with complete decoupling from protons, with selective decoupling from protons (off-resonance mode), and without decoupling from protons. The chemical shifts were measured relative hexamethyldisiloxane, $CHCl_3$, or CH_2Cl_2 (^1H, δ 0.04, 7.24, and 5.33 ppm, respectively) and $CDCl_3$ or CD_2Cl_2 (^{13}C, δ_C 76.9 and 53.3 ppm, respectively) for neutral compounds and relative to CH_2Cl_2 and CD_2Cl_2 or $CHCl_3$ and $CDCl_3$ for cations. The IR spectra were recorded on a UR-20 spectrometer, and

*** With participation of N.V. Kochubei.

the UV spectra were measured on a Specord UV-Vis spectrophotometer. The molecular weights and elemental compositions of the newly synthesized compounds were determined from the high-resolution mass spectra which were obtained on a Finnigan MAT 8200 instrument.

Doubly distilled HSO_3F (bp 158–161°C) and trifluoromethanesulfonic acid from Fluka were used for generation of carbocations. Samples for NMR analysis were withdrawn according to the procedure described in [13]. The properties of compounds synthesized by known methods were consistent with published data. The heats of formation were calculated by the MINDO/3 method using MOPAC software [14].

2-Bromobiphenyl was synthesized by the procedure reported in [15] from 2-aminobiphenyl which was prepared in quantitative yield by reduction of 2-nitrobiphenyl [16] at 60°C with hydrazine hydrate in alcohol [17] or with hydrogen (30 atm) over IKT-3-20 (5% of Pd/C) as catalyst (cf. [17, 18]). The ^1H and ^{13}C NMR spectra of the product (2-bromobiphenyl) coincided with those given in [19].

3-(2-Biphenylyl)-1,2,3-trimethyl-4-methylenecyclobuten (V). A solution of 4.06 g (27.06 mmol, 95% purity) of 3-chloro-1,2,3-trimethyl-4-methylenecyclobutene (**X**) [20] in 10–15 ml of ether was added dropwise over a period of 10–15 min with stirring at room temperature to a solution of Grignard compound prepared by standard procedure from 0.724 g of magnesium (activated by iodine vapor) in 20 ml of ether and a solution of 6.94 g (29.77 mmol) of 2-bromobiphenyl in 15–20 ml of ether. The mixture was heated for 1 h under reflux (on a water bath) to complete the reaction, cooled to 0°C, and quenched by addition of 7 ml of water. The yellow ether layer was separated by decanting, and the aqueous phase was extracted with three portions of ether, each time the ether layer being separated by decanting. The ether extracts were combined and evaporated at 50°C, the residue was treated with 30 ml of pentane, the precipitate was filtered off, and the filtrate was evaporated at 50–60°C to obtain 7.86 g of a darkish liquid which, according to the ^1H NMR data, was the target compound containing some impurities. The pure product was isolated by sublimation from several portions of the liquid under reduced pressure (1 mm) in a sublimator equipped with a finger condenser to which a small cup (empty hemisphere) was attached through a short arm to collect cyclobutene **V**. The latter condensed onto the condenser and fell into the cup at a temperature exceeding by 10–25°C the temperature of sublimation of biphenyl under the given residual pressure (72–74°C; biphenyl was separated preliminarily). The sublimation process was terminated when first crystals of compound **VII** (which sublimes at 100–115°C) appeared on the outer cup surface. The yield of compound **V** was 55% on the initial cyclobutene **X**. ^1H NMR spectrum (10% solution in $CDCl_3$, 200.13 MHz), δ, ppm: 1.67 s (3H, 3-CH_3), 1.57 (3H) and 1.74 (3H) (1-CH_3, 2-CH_3; broadened signals due to quadruplet coupling with each other; J = 1.2 Hz), 4.57 s (2H, =CH_2), 7.2–7.8 m (9H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$, 10% solution), δ_C, ppm: 8.6 q and 10.0 q (1-, 2-CH_3); 23.6 q (3-CH_3); 56.3 s (C^3); 90.7 t (=CH_2); 126.2 d and 129.1 d (2C each, $C^{2''}$, $C^{6''}$, $C^{3''}$, $C^{5''}$); 125.2 d, 125.9 d, 126.7 d, 128.0 d, 132.0 d ($C^{3'}$–$C^{6'}$, $C^{4''}$); 139.7 s, 140.2 s, 142.1 s, 143.6 s, 153.7 s, 159.5 s (C^1, $C^{2'}$, C^4, $C^{1'}$, $C^{2'}$, $C^{1''}$). Found, m/z: $[M]^+$ 260.1565. $C_{20}H_{20}$. Calculated: M 260.1565.

1,2,2a,10b-Tetramethyl-2a,10b-dihydrocyclobuta[*l*]phenanthrene (VII) was synthesized by a procedure analogous to that described in [1] for the preparation of 6b,7,8,8a-dihydrocyclobut[*a*]acenaphthylene. Yield 61%. mp 153–154°C (from hexane). ^1H NMR spectrum ($CDCl_3$, 400.13 MHz), δ, ppm: 1.51 s (6H) and 1.55 s (6H, CH_3), 7.21–7.30 m (4H, 4-H, 5-H, 8-H, 9-H), 7.38–7.42 m (2H, 3-H, 10-H), 7.97–8.01 m (2H, 6-H, 7-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 8.3 q (1-CH_3, 2-CH_3); 21.2 q (2a-CH_3, 10b-CH_3); 48.9 s (C^{2a}, C^{10b}); 123.0 d, 125.9 d, 127.2 d, 127.4 d (C^3–C^6, C^7–C^{10}); 130.1 s, 140.4 s, 141.5 s (C^1, C^2, C^{2b}, C^{10a}, C^{6a}, C^{6b}). UV spectrum (ethanol), λ_{max}, nm (log ε): 218 (4.63), 232 (4.16), 242 (4.01), 272 (4.12), 284 (4.11), 300 (3.70), 311 (3.81). IR spectrum (CCl_4, 3% solution), ν, cm^{-1}: 1040 m, 1060 m, 1375 m, 1380 m, 1440 s, 1450 m, 1495 m, 2915 m, 2940 m, 2970 m, 2995 m, 3070 m. Found, m/z: $[M]^+$ 260.1567. $C_{20}H_{20}$. Calculated: M 260.1565.

4-(2-Biphenylyl)-1,2,3,4-tetramethylcyclobutenyl cation (IV). A mixture of 0.1 ml of superacid (HSO_3F or an equimolar mixture of HSO_3F and SbF_5, diluted with three volumes of HSO_3F) and two volumes of SO_2ClF as diluent was placed in an NMR ampule, thoroughly stirred, and cooled to –130°C, a layer of SO_2ClF (1–2 volumes) was condensed thereonto, and then a suspension of precursor **V** (45–75 mg) in one volume of SO_2ClF and/or one volume of CD_2Cl_2 was layered on the top (after layering, the mixture remained colorless). The mixture was stirred with a glass rod cooled with liquid nitrogen to obtain a red solution with a purple–crimson shade. The mixture was filtered (by breaking the bottom of the ampule) at –130°C through a small layer of mineral

wool into another NMR ampule which was preliminarily connected to the first one.

***trans*- and *cis*-4,5,6,6-Tetramethyl-4,5,6-trihydrocyclopenta[*j,k*]phenanthren-5-yl cations VIa and VIb.** *a*. A mixture of cations **VIa** and **VIb** was initially generated by adding powdered compound **VII** (2–3 mmol), cooled to –85°C, to 70–80 mmol of HSO_3F cooled to –85°C. The mixture was stirred and kept for 5 min at –50°C, and a small amount of CD_2Cl_2 was added to stabilize conditions for recording NMR spectra. According to the ^{1}H NMR spectrum (–40°C, 200.13 MHz), the ratio of **VIa** and **VIb** was 1:2. The spectrum contained the following nonoverlapped signals, δ, ppm: cation **VI**: 3.60 q (1H, 4-H, *J* = 7 Hz), 3.73 q (1H, 5-H, *J* = 7 Hz); cation **VIb**: 4.05 q.d (1H, 4-H, *J* = 7, 3 Hz), 4.32 q.d (1H, 5-H, *J* = 7, 3 Hz); partially overlapped signals: **VIa**: 1.71 d (4-CH_3, *J* = 7 Hz), 1.98 s and 2.07 s (6-CH_3); **VIb**: 1.64 d (4-CH_3, *J* = 7 Hz), 1.79 d (5-CH_3, *J* = 7 Hz), 1.99 s and 2.05 s (6-CH_3); the spectrum also contained unresolved multiplets from aromatic protons of both isomers at δ 7.7–8.7 ppm and the 5-CH_3 signals of isomer **VIa** at δ 1.9–2.0 ppm. The ^{13}C NMR spectrum of the same solution (–40°C) contained the following signals, δ_C, ppm: **VIb**: 15.3 q (4-CH_3), 15.6 q (5-CH_3), 25.9 q and 28.8 q (6-CH_3), 45.9 d (C^4), 54.7 d (C^5), 50.6 s (C^6), 122.8 d (C^1), 125.8 d (C^3), 126.5 d (C^{10}), 127.3 d (C^7), 128.7 d (C^9), 133.6 d (C^8), 126.6 s (C^{10a}), 138.1 s (C^{10c}), 145.1 s (C^{10b}), 149.8 s (C^{6a}), 174.4 s (C^{3a}), 155.1 d (C^2), 241.5 s (C^{5a}); **VIa**: 15.2 q (4-CH_3), 15.9 q (5-CH_3), 27.0 q and 27.1 q (6-CH_3), 49.7 d (C^4), 59.4 d (C^5), 50.0 s (C^6), 125.4 d, 127.5 d, 138.4 s, 145.4 s, 150.5 s, 173.1 s, 155.6 d (C^2), 239.8 s (C^{5a}); the other singlet and doublet signals from sp^2-carbon atoms were obviously overlapped with those of **VIb**.

b. A similar mixture containing cations **VIa** and **VIb** was obtained (according to the NMR data) by heating solutions of **IV** from –130 to –36°C, as well as by heating from –130 to –36°C of a sample prepared by dissolution at –130°C of a mixture of 45 mg of compound **VII** with two volumes of SO_2ClF and one volume of CD_2Cl_2 in HSO_3F (0.1 ml) diluted with two volumes of SO_2ClF.

***trans*-4,5,6,6-Tetramethyl-4,5,6-trihydrocyclopenta[*j,k*]phenanthren-5-yl cation (VIa).** A solution of 0.063 g of compound **VII** in 0.3 ml of $CDCl_3$ was added with stirring at room temperature to a mixture of 0.5 ml of trifluoromethanesulfonic acid and 0.3 ml of $CDCl_3$. According to the ^{1}H and ^{13}C NMR spectra, the resulting dark violet solution contained cation **VIa** (cf. the spectral data for known 9,10-disubstituted phenanthrenylium ions; see references in [7]). ^{1}H NMR spectrum (20°C, 200.13 MHz), δ, ppm: 1.60 d (3H, 4-CH_3, *J* 7 = Hz), 1.85 d (3H, 5-CH_3, *J* = 7 Hz), 1.89 s (3H) and 1.96 s (3H) (6-CH_3), 3.49 q (1H, 4-H, *J* = 7 Hz), 3.62 q (1H, 5-H, *J* = 7 Hz), 7.66 t (1H, 9-H), 7.76 d (1H, 3-H), 7.78 t (1H, 8-H, *J* = 8 Hz), 7.93 d (1H, 7-H, *J* = 8 Hz), 8.33 d (1H, 1-H, *J* = 7 Hz), 8.41 d (1H, 10-H, *J* = 8 Hz), 8.60 t (1H, 2-H, *J* = 7 Hz). ^{13}C NMR spectrum (20°C), δ_C, ppm: 16.0 q.q (4-CH_3, ^1J = 130, ^3J = 5 Hz); 16.6 q.q (5-CH_3, ^1J = 130, ^3J = 5 Hz); 27.1 q.d.d (^1J = 130, ^2J = 6, ^3J = 3 Hz) and 28.2 q.d.d (^1J = 130, ^2J = 6, ^3J = 3 Hz) (6-CH_3); 49.9 d.m (C^4, ^1J = 130 Hz); 59.2 d.m (C^5, ^1J = 125 Hz); 50.3 s (C^6); 122.9 (C^1), 125.3 (C^3), 126.6 (C^{10}), 127.2 (C^7), 129.0 (C^9), and 134.1 (C^8) (d.d each, ^1J = 163, ^3J = 8 Hz); 126.2 s (C^{10a}); 138.3 s (C^{10c}); 145.8 s (C^{10b}); 150.4 s (C^{6a}); 172.7 s (C^{3a}); 155.6 d (C^2, ^1J = 163 Hz); 239.2 s (C^{5a}) (^{13}C–^{1}H coupling constants are given).

9-Methyl-9-(*cis*-1-methyl-1-propenyl)-10-methylene-9,10-dihydrophenanthrene (VIII). A solution of 0.5 g (1.9 mmol) of olefin **VII** in 2 ml of CH_2Cl_2 was added dropwise over a period of 20 min to a solution of 1.0 ml (17.4 mmol) of HSO_3F in 5 ml of SO_2ClF, stirred at –100°C under argon. The resulting dark crimson solution was added dropwise over a period of 30 min to a suspension of 5.4 g (51 mmol) of Na_2CO_3 in a mixture of 7.4 ml (5.3 mmol) of triethylamine, 5 ml of methanol, and 70 ml of dry ether under vigorous stirring at –100°C. The mixture was stirred for 2 h, allowing it to gradually warm up to room temperature. The liquid part was separated by decanting, filtered through a small layer of Al_2O_3, washed with a 10% solution of Na_2CO_3, dried over K_2CO_3, and evaporated under reduced pressure to obtain 0.46 g of an oily substance which, according to the NMR spectra, was a mixture of approximately equal amounts of compounds **VIII** and **IX**. Pure product **VIII** was isolated by column chromatography on Al_2O_3 using hexane as eluent. ^{1}H NMR spectrum ($CDCl_3$, 400.13 MHz), δ, ppm: 1.43 quint (3H, 1-CH_3, *J* = 1.2 Hz), 1.49 s (3H, 9-CH_3), 1.58 d.q (3H, CH_3C=, *J* = 6.7, 1.1 Hz), 5.38 q.q (1H, CH_3C**H**=, *J* = 6.7, 1.2 Hz), 5.15 s (1H, =CH_2), 5.49 s (1H, =CH_2), 7.19–7.35 m (5H, 2-H, 3-H, 6-H, 7-H, 8-H), 7.56 d.d (1H, 1-H, *J* = 7.6, 1.7 Hz), 7.74–7.82 m (2H, 4-H, 5-H); the *cis* configuration of the 1-methyl-1-propenyl fragment follows from the value of $^5J_{HH}$ equal to 1.2 Hz [21]. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.6 q, 15.6 q, 26.4 q, 51.4 s, 111.2 t, 120.9 d, 122.9 d, 123.4 d, 125.8 d, 126.5 d, 127.0 d, 127.6 d, 127.7 d, 128.2 d, 132.1 s, 132.8 s, 134.9 s, 139.3 s,

142.5 s, 149.8 s (cf. [22]). Found, *m*/*z*: $[M]^+$ 260.1557. $C_{20}H_{20}$. Calculated: *M* 260.1565.

4,5,6,6-Tetramethyl-4,6-dihydrocyclopenta[*j*,*k*]-phenanthrene (IX). A solution of 0.19 g (0.73 mmol) of olefin **VII** in 0.9 ml of $CHCl_3$ was added dropwise over a period of 10 min to an emulsion formed by 1.5 ml (17 mmol) of CF_3SO_3H and 0.9 ml of $CHCl_3$, which was stirred at room temperature under argon. The resulting dark crimson solution was added dropwise over a period of 30 min under vigorous stirring to a suspension of 3.6 g (34 mmol) of Na_2CO_3 in a mixture of 5 ml of triethylamine and 70 ml of hexane. The mixture was stirred for 30 min and filtered through a small layer of Al_2O_3, the precipitate was washed with 40 ml of ether, and the filtrate was evaporated under reduced pressure to obtain 0.19 g of an oily substance which was almost pure olefin **IX**. ^1H NMR spectrum ($CDCl_3$, 400.13 MHz), δ, ppm: 1.55 (4-CH_3), 1.94 (6-CH_3), 1.95 (6-CH_3), 1.94 (6-CH_3), 2.44 (5-CH_3), 3.46 (4-H), 7.42 (2-H), 7.47 (3-H), 7.48 (9-H), 7.50 (8-H), 7.76 (7-H), 7.93 (1-H), 8.15 (10-H); J_{HH}, Hz: 4-CH_3–4-H 7.5, 5-CH_3–4-H 0.9, 1-H–2-H 7.8, 1-H–3-H 0.7, 1-H–10-H 0.5, 2-H–3-H 7.4, 3-H–4-H 0.9, 7-H–8-H 8.0, 7-H–9-H 1.3, 7-H–10-H 0.5, 8-H–9-H 7.3, 8-H–10-H 1.5, 9-H–10-H 7.8. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.7 q, 15.6 q, 30.8 q, 30.8 q, 37.0 s, 48.5 d, 118.6 d, 121.2 d, 121.8 d, 124.7 d, 125.5 s, 126.0 d, 127.3 d, 127.4 d, 130.3 s, 138.3 s, 140.1 s, 141.2 s, 145.7 s, 146.4 s. Found, *m*/*z*: $[M]^+$ 260.1562. $C_{20}H_{20}$. Calculated: *M* 260.1565.

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