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Long-Lived Carbocations: Generation from 5,5,10,10-Tetramethyl-5,10-dihydroindeno[2,1-*a*]indene, Structure, and Rearrangements

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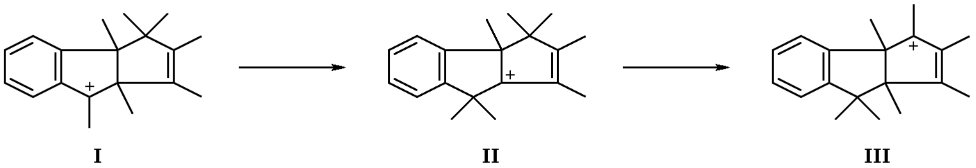
Abstract—According to the NMR data, protonation of 5,5,10,10-tetramethyl-5,10-dihydroindeno[2,1-*a*]indene in the system HSO_3F–SO_2ClF–CD_2Cl_2 at –80°C gives rise to long-lived 5,5,10,10-tetramethyl-2*H*-5,10-dihydroindeno[2,1-*a*]indenium ion which undergoes isomerization into 4b,5,10,10-tetramethyl-4b,5,9b,10-tetrahydroindeno[2,1-*a*]inden-5-yl cation on raising the temperature. On the basis of the data obtained for rearrangements of such carbocations an alternative mechanism has been proposed for the rearrangements of structurally related carbocations having a bicyclo[3.3.0]octane skeleton.

In the recent years, chemical behavior of polycyclic aromatic hydrocarbons and their derivatives in superacidic media attracts increased interest [1] which is explained, in particular, by their specific role in carcinogenesis and environmental pollutions and also by new prospects in fine organic synthesis, originating from cationoid molecular rearrangements of these compounds. Among polycyclic hydrocarbons, there is a considerable interest in poorly studied compounds having a benzopentalene skeleton. The presence of a fused aromatic ring is expected to restrict possible rearrangement processes, thus ensuring a fairly high regioselectivity. Using ^1H and ^{13}C NMR spectroscopy, we previously found [2] that long-lived 1,1,2,3,3a,4,8b-heptamethyl-1,3a,8b-trihydrobenzopentalenium ion (**I**), generated in the system HSO_3F–SO_2ClF at –50°C, undergoes rearrangement into 1,1,2,3,4,4,8b-heptamethyl-1,4,8b-trihydrobenzopentalenium ion (**II**). When the acid system HSO_3F–SO_2ClF was replaced by CF_3SO_3H and the temperature was raised to 20°C, we observed a more profound rearrangement, namely the transformation of cation **II** into 1,2,3,3a,4,4,8b-heptamethyl-3a,4,8b-trihydrobenzopentalenium ion (**III**) (Scheme 1); the latter did not change under these conditions.

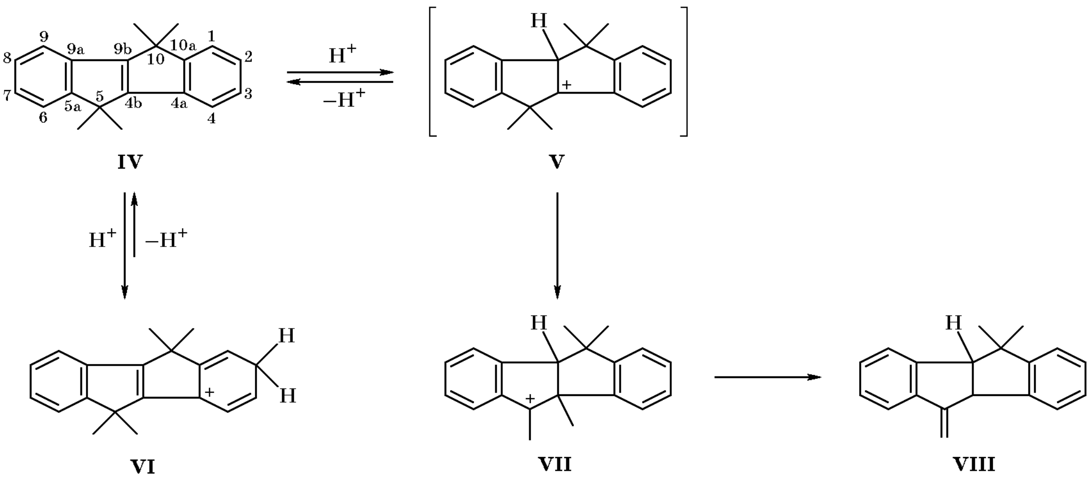
With the goal of revealing general relations holding in cationic rearrangements of benzopentalene derivatives in superacidic media we examined the behavior of 5,5,10,10-tetramethyl-5,10-dihydroindeno[2,1-*a*]indene (**IV**). We expected that compound **IV** is sufficiently basic to ensure displacement of the acid–base equilibrium toward long-lived 5,5,10,10-tetramethyl-4b,5,9b,10-tetrahydroindeno[2,1-*a*]inden-4b-yl cation (**V**). The presence of two fused benzene rings in molecule **IV** should restrict the number of rearrangement processes even more strongly, and those actually occurring should appear similar to the processes described in [2] for related carbocations having only one fused benzene ring.

Using NMR spectroscopy, we have found that dissolution of compound **IV** in the acid system

Scheme 1.



Scheme 2.



$HSO_3F–SO_2ClF–CD_2Cl_2$ (1 : 7 : 1, by volume) at –80 to –70°C gives rise not to the expected cation **V** but to 5,5,10,10-tetramethyl-2*H*-5,10-dihydroindeno-[2,1-*a*]indenium ion (**VI**) (Scheme 2).

In the ^1H NMR spectrum of the resulting solution, recorded at –75°C, we observed a signal at δ 4.17 ppm from methylene protons. Its multiplicity (a triplet with a coupling constant of 3.5 Hz) suggests that proton adds to molecule **IV** at a position to which two hydrogen atoms are neighboring. The ^{13}C NMR spectrum contains 8 singlet signals, 7 doublets, a triplet, and 2 quartets; the presence of three downfield singlets at δ_C 202.8, 169.2, and 167.6 ppm indicates delocalization of the positive charge over extended π system including the double bond and nonprotonated aromatic ring (cation **VI**). The results of *ab initio* calculations with the 6-31G basis set suggest a planar structure of the cation, which provides effective charge delocalization.

Apart from cation **VI**, we observed formation of isomeric 4b,5,10,10-tetramethyl-4b,5,9b,10-tetrahydroindeno[2,1-*a*]inden-5-yl cation (**VII**) (–80 to –70°C, 8 h*; Scheme 2). According to the NMR data, the ratio of ions **VII** : **VI** at –75°C increases in 83 min from 0.9 : 1.1 to 1.1 : 0.9, which corresponds to $\Delta G^{\neq}$ = 65 kJ/mol. As the temperature rises to –37°C, only signals of cation **VII** remain in the ^1H NMR spectrum. Cation **VII** is also formed on dissolution of compound **IV** in CF_3SO_3H at 20°C.** In the ^1H NMR spectrum we observed 4 signals from methyl protons, a signal from CH proton, and 8 signals from aromatic protons. In the ^{13}C NMR spectrum 7 singlets, 9 doublets, and 4 quartets were present. The positions of the downfield signal from methyl protons in the ^1H NMR spectrum (δ 3.59 ppm) and of the signal from carbocationic center in the ^{13}C NMR spectrum (δ_C 254.8 ppm) are typical of benzyl-like cations [2]. The presence of an additional splitting of the signals from geminal methyl groups with a coupling constant typical of a C–C–C–H fragment and the absence of such splitting for the methyl group attached to the cationic center are consistent with the location of hydrogen at C^{9b} and of methyl group at C^{4b}. These data led us to assign structure **VII** to the above cation.

Neutralization of a solution of cation **VII** in CF_3SO_3H with a suspension of Na_2CO_3 in pentane at 0°C gave compound **VIII**. In keeping with the ^1H and ^{13}C NMR data, compound **VIII** contains 20 carbon atoms, two *ortho*-phenylene moieties, a $C=CH_2$ fragment, a bridgehead hydrogen atom, and three methyl groups. The aromatic protons in molecule **VIII** resonate over a wide range, and one of the $=CH_2$ protons gives a relatively downfield signal. These data indicate that the product formed by neutralization of cation **VII** is an olefin resulting from elimination of proton from methyl group. Obviously, specific features of the ^1H NMR spectrum of this product are explained by location of the $C=CH_2$ fragment in the α-position with respect to the aromatic ring (cf. [2]).

The results of the present study in combination with the data on the transformations **I** → **II** → **III** (Scheme 1) led us to conclude that 1,2-shift of methyl group readily occurs in carbocations having a pentalene fragment. On the basis of this conclusion we can explain distribution of deuterium in ion **IX**,

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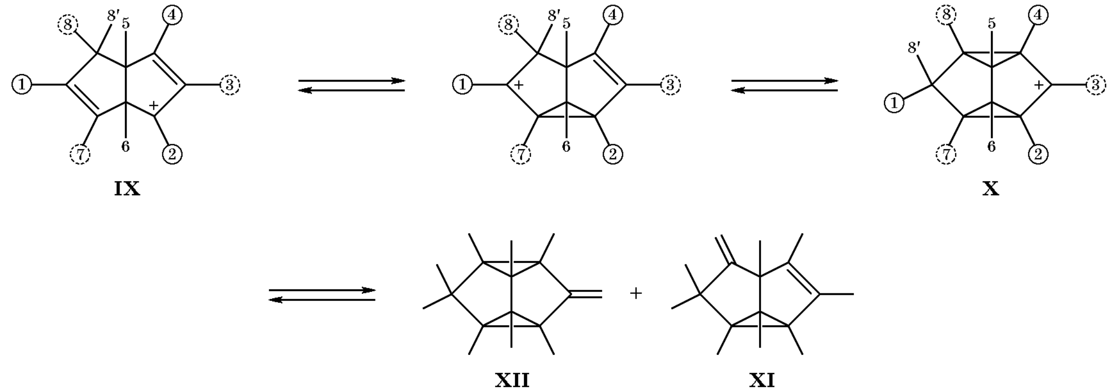
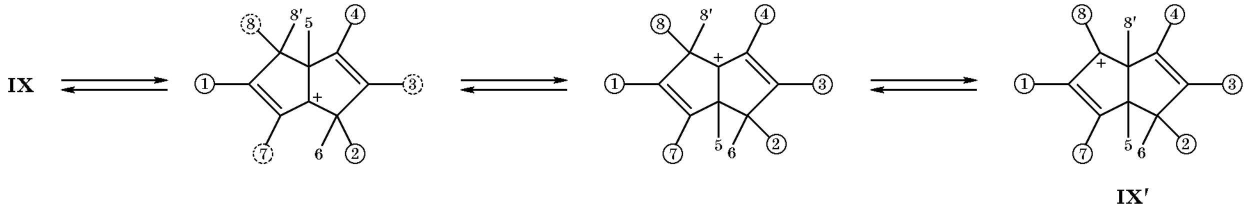
* The poor solubility of compound **IV** in the given superacidic system is responsible for the long time of the process.

** Unlike HSO_2F, CF_3SO_3H does not sulfonate aromatic compounds.

Scheme 3.



Scheme 4.



given in [3] (Scheme 3; the atom numbering in Schemes 3 and 4 corresponds to that given in [3]). According to [3], in CF_3COOD at room temperature ion **IX** having CD_3 groups in positions *1*, *2*, and *4* and partially deuterated methyl groups in positions *3*, *7*, and *8* is converted into the ion with completely deuterated methyl groups in all the positions listed above; the rates of isotope exchange in the 3-, 7-, and 8-CH_3 groups are approximately equal. A possible mechanism of the process [3] is shown in Scheme 3. Although Scheme 3 does not exclude coincidence of the rates of deuterium exchange in different CH_3 groups (in positions *3*, *7*, and *8*), we believe that Scheme 4 is preferred. Similar amounts of deuterium in positions *3*, *7*, and *8* of ion **IX** is a necessary result of the mechanism shown in Scheme 4, provided that the rate of degenerate rearrangement of **IX** is considerably lower than the rate of H–D isotope exchange in methyl groups in positions *1*, *2*, and *4*.

EXPERIMENTAL

The NMR spectra were recorded on Bruker AC-200 and Bruker DRX-500 spectrometers. Deuterated methylene chloride (CD_2Cl_2) was used as internal reference in acid solutions (δ 5.33 ppm, δ_C 53.6 ppm). The spectra of neutral compounds were obtained from solutions in CCl_4–$(CD_3)_2CO$ (1 : 3, by volume); the chemical shifts were measured relative to the signals of $(CD_3)_2CO$ (δ 2.04 ppm; δ_C 29.8 ppm). The following reagents and solvents were used: technical-grade HSO_3F was distilled twice, bp 162°C; SO_2ClF was prepared as described in [4] and was purified by passing the gaseous substance through concentrated sulfuric acid; CF_3SO_3H (Fluka) was of pure grade; pentane was of pure grade; and Na_2CO_3 was of chemically pure grade.

5,5,10,10-Tetramethyl-5,10-dihydroindeno[2,1-*a*]indene (IV) was synthesized from 5,5,10,10-tetramethyl-4b,5,9b,10-tetrahydroindeno[2,1-*a*]indene [5] according to the procedure described in [6]. For ^{1}H NMR spectrum, see [6]. ^{13}C NMR spectrum, δ_C, ppm: 24.8 q, 45.0 s, 119.4 d, 121.9 d, 124.9 d, 126.7 d, 137.9 s, 155.5 s, 158.8 s.

Quantum-chemical calculations. Geometric parameters of cation **VI** were optimized using the 6-31G basis set with the aid of GAMESS program [7] and were then used to calculate ^{13}C chemical shifts (IGLO program [8], DZ basis set). Calculated ^{13}C NMR spectrum of cation **VI**, δ_C, ppm: 145.9 (C^1), 26.8 (C^2), 168.4 (C^3), 121.0 (C^4), 177.7 (C^{4a}), 145.1 (C^{4b}), 29.7 (C^5), 167.8 (C^{5a}), 123.0 (C^6), 148.0 (C^7), 128.8 (C^8), 134.1 (C^9), 125.3 (C^{9a}), 218.8 (C^{9b}), 30.8 (C^{10}), 144.7 (C^{10a}), 21.4 (5-CH_3), 20.8 (10-CH_3).

Generation of carbocations. *a. Mixture of ions VI and VII.* To a solution of 0.1 ml of HSO_3F in

0.7 ml of SO_2ClF at –95°C we added 40 mg of olefin **IV** and 0.1 ml of CD_2Cl_2. The mixture was stirred at –80 to –70°C* until it became homogeneous (8 h), and the resulting dark green solution containing ions **VI** and **VII** was transferred into an NMR ampule. ^{1}H NMR spectrum of **VI** ($HSO_3F–SO_2ClF–CD_2Cl_2$, –75°C), δ, ppm: 1.70 s (6H, 5-CH_3 or 10-CH_3), 1.77 s (6H, 10-CH_3 or 5-CH_3), 4.17 t (2H, 2-H, *J* = 3.5 Hz), 7.6–8.2 m (7H, 1-H, 3-H, 4-H, 6-H, 7-H, 8-H, 9-H). ^{13}C NMR spectrum, δ_C, ppm: 22.7 q (10-CH_3 or 5-CH_3), 23.4 q (5-CH_3 or 10-CH_3), 38.9 t (C^2), 45.8 s (C^5 or C^{10}), 47.0 s (C^{10} or C^5), 124.6 d (C^4 or C^6), 124.7 d (C^6 or C^4), 128.0 d (C^8 or C^9), 129.9 d (C^9 or C^8), 134.3 s (C^{9a}), 138.0 d (C^1 or C^7), 146.3 d (C^7 or C^1), 159.1 s (C^{10a} or C^{4b}), 159.3 s (C^{4b} or C^{10a}), 164.3 d (C^3), 167.6 s (C^{5a} or C^{4a}), 169.2 s (C^{4a} or C^{5a}), 202.8 s (C^{9b}) (the signals were assigned on the basis of the calculated spectrum). The NMR spectra of ion **VII** in $HSO_3F–SO_2ClF–CD_2Cl_2$ at –75 and –37°C were almost identical to those recorded in CF_3SO_3H at 20°C (see below).

b. Ion ***VII***. To 0.4 ml of CF_3SO_3H at 0°C we added 40 mg of olefin **IV** and 0.05 ml of CD_2Cl_2. The mixture was stirred for several minutes, and the resulting dark red solution was transferred into an NMR ampule. ^{1}H NMR spectrum (CF_3SO_3H, 20°C), δ, ppm: 1.19 s (3H, 10-CH_3), 1.78 s (3H, 10-CH_3), 2.11 s (3H, 4b-CH_3), 3.59 d (3H, 5-CH_3, *J* = 1 Hz), 4.16 s (1H, 9b-H), 7.26 d.d (1H, 1-H or 4-H, *J* = 8, 1 Hz), 7.51 t.d (1H, 3-H or 2-H, *J* = 8, 1 Hz), 7.56 t.d (1H, 2-H or 3-H, *J* = 8, 1 Hz), 7.70 d.d (1H, 4-H or 1-H, *J* = 8, 1 Hz), 7.96 t (1H, 7-H, *J* = 8 Hz), 8.16 d (1H, 9-H, *J* = 8 Hz), 8.56 d (1H, 6-H, *J* = 8 Hz), 8.64 t (1H, 8-H, *J* = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 23.7 q (5-CH_3, *J* = 131 Hz), 26.2 q.d (4b-CH_3, *J* = 132, 3 Hz), 27.2 q.m (10-CH_3, *J* = 128 Hz), 34.7 q.m (10-CH_3, *J* = 128 Hz), 46.9 m (C^{10}), 71.9 d.m (C^{9b}, *J* = 139 Hz), 76.1 m (C^{4b}), 125.1 d.d (C^1–C^4, *J* = 158, 8 Hz), 125.9 d.d (C^1–C^4, *J* = 160, 8 Hz), 130.2 d.d (C^1–C^4, *J* = 163, 8 Hz), 133.0 d.d (C^1–C^4, *J* = 162, 8 Hz), 132.1 d.d (C^9, *J* = 169, 7 Hz), 133.9 d.d (C^7, *J* = 169, 7 Hz), 137.4 m (C^{4a}, C^{5a}, or C^{10a}), 137.8 d.d (C^8 or C^6, *J* = 169, 8 Hz), 144.2 m (C^{5a}, C^{10a}, or C^{4a}), 153.2 m (C^{10a}, C^{4a}, or C^{5a}), 155.8 d.d (C^6 or C^8, *J* = 164, 8 Hz), 179.1 m (C^{9a}), 254.8 m (C^5).

Neutralization of the acid solution of ion VII. A solution of ion **VII** trifluoromethanesulfonate, prepared as described above, was added to a suspension of 2 g of finely powdered Na_2CO_3 in 50 ml of pentane, vigorously stirred at 0°C. The mixture was filtered through a layer of Al_2O_3, and the solution was evaporated. According to the NMR data, the residue (40 mg) was almost pure olefin **VIII**. ^{1}H NMR spectrum, δ, ppm: 0.71 s (3H), 1.51 s (3H), 1.55 s (3H), 3.37 s (1H), 5.06 s (1H), 5.42 s (1H), 6.9–8.5 m (8H). ^{13}C NMR spectrum, δ_C, ppm: 29.6 q, 29.5 q, 31.6 q, 46.0 s, 59.0 s, 69.1 d, 103.3 t, 121.4 d, 122.8 d, 123.5 d, 126.4 d, 127.1 d, 127.4 d, 127.5 d, 128.5 d, 140.8 s, 144.4 s, 146.1 s, 152.1 s, 157.6 s.

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* No dissolution occurred at a lower temperature.