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REARRANGEMENTS OF LEDENE AND AROMADENDRENE IN SUPERACIDS

Marina P. Polovinka[a], Andrei A. Shal'ko[a], Dina V. Korchagina[a], Yurii V. Gatilov[a], Vladimir V. Shcherbukhin[b], Vladimir A. Barkhash[a]

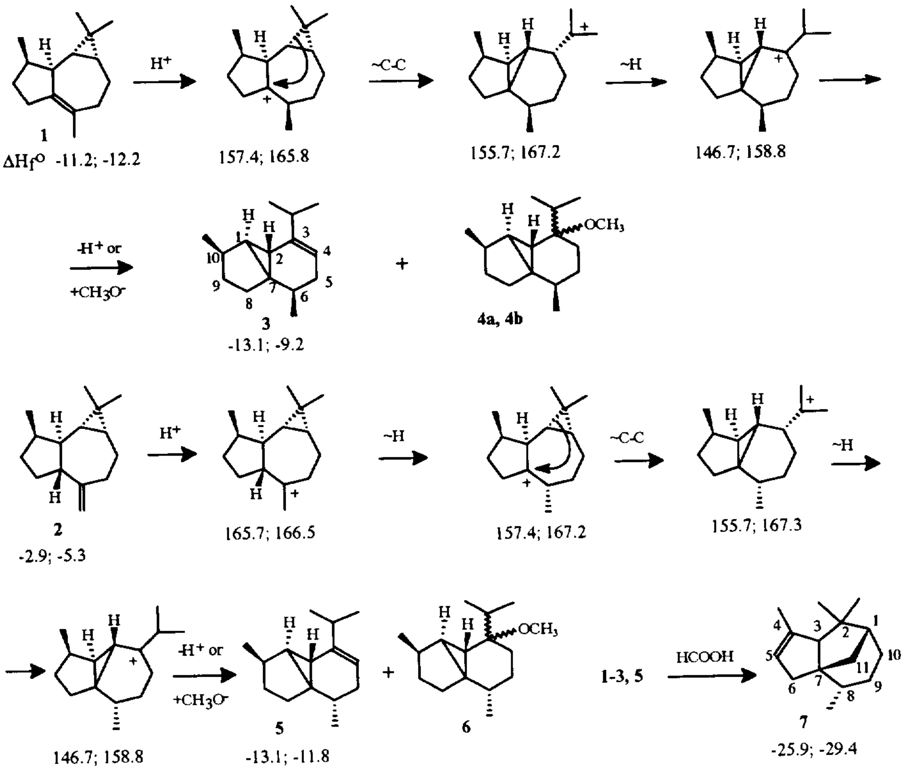
[a]Novosibirsk Institute of Organic Chemistry, Novosibirsk 630090, Russia
[b]Institute of Organic Chemistry, Moscow 117913, Russia

Abstract: Acid-catalyzed rearrangements of ledene and aromadendrene were studied for the first time. In superacidic media, conversion into compounds with the natural cubebane skeleton was discovered. A marked difference between the compositions of the conversion products of one and the same olefin in superacids and in ordinary acidic media was observed.

Data on acid-catalyzed rearrangements of ledene **1** and aromadendrene **2** are virtually absent from literature. We showed that the dissolution of the olefin **1** in HSO_3F—SO_2FCl [the HSO_3F/**1** molar ratio is 17:1; the SO_2FCl/HSO_3F volume ratio is 4:1, at -110 – -115°C] or in SbF_5—HSO_3F—SO_2FCl (the SbF_5/HSO_3F molar ratio is 1:5.5) with subsequent "quenching" of the acidic solution by the CH_3OH—$(C_2H_5)_2O$ mixture produces a mixture of three compounds — the olefin **3** and the methyl ethers **4a** and **4b** with the contents 28, 15, and 52%, respectively (GLC). Chromatography on 20% $AgNO_3$—SiO_2 makes it possible to isolate (1R,2S,6R,7S,10R)-3-isopropyl-6,10-dimethyltricyclo[5.3.0.0^{2,7}]dec-3-ene **3** with the yield 46%, whereas the ethers **4a** and **4b** decompose. The latter compounds were isolated with the yield 57% by chromatography of the reaction mixture on Al_2O_3; chromatography of the ethers **4a**, **4b** on SiO_2 produces the olefin **3** with the yield 42%. Similarly, two products (**5** and **6**) were obtained from the olefin **2** with the contents 18 and 65%, respectively (GLC). Chromatography on a column with 20% $AgNO_3$—SiO_2 (with the use of hexane as the eluent) produced (1R,2S,6S,7S,10R)-3-isopropyl-6,10-dimethyltricyclo[5.3.0.0^{2,7}]dec-3-ene **5** with the yield 26%. The second compound, according to ^{1}H NMR spectra of the reaction mixture, is (1R,2S,6S,7S,10R)-3-methoxy-3-isopropyl-6,10-dimethyltricyclo[5.3.0.0^{2,7}]-decane **6**, which is converted to the olefin **5** during chromatography on SiO_2.

Comparing the products of rearrangements of the olefins **1** and **2** in media with different acidities, we see that these reactions proceed according to intramolecular mechanisms; the latter mechanisms were suggested and theoretically analyzed in accordance with the approach described in Ref. 1.

Computer-generated schemes of rearrangements of the olefins **1** and **2** are relatively simple (see the scheme). Under the structural formulas in the scheme, the heats of formation ΔH_f^o(gas) in kcal mol^{-1} are given; the first values were calculated by the MMX program, the second, by the MNDO program (the AM1 method for ions and PM3 for olefins). Boiling of compounds **1**–**3**, **5** in formic acid results in the formation of (1R,3S,7S,8S)-2,2,4,8-tetramethyltricyclo- [5.3.1.0^{3,7}]undec-4-ene **7** as the principal product (up to 80%, GLC). Thus, products of rearrangement differ greatly even for one and the same olefin in superacidic and "ordinary" acidic media (cf. Ref. 2). Compounds **3**–**7** have not been described in literature, although the molecules **3**–**6** have the natural cubebane skeleton. The structures of all the resultant compounds were established by ^{1}H and ^{13}C NMR spectra, including 2D spectra of ^{13}C-^{13}C correlation[3-5].



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3. Analytical data for **3**: $[\alpha]^{20}_{580}$ +157.8° (c 19.9, $CHCl_3$); HRMS m/e for $C_{15}H_{24}$: calcd. 204.1878, obsd. 204.1876. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 0.87 (m, H-9), 0.92 (d, J 6.5, CH_3-14), 1.01 (d, J 6.5, CH_3-15), 1.01(d, J 2.5, H-2), 1.04 and 1.06 (d, J 7, CH_3-12 and CH_3-13), 1.28 (dd, J 4, 2.5, H-1), 1.64 (ddd, J 13, 8, 8, H-9), 1.68 (ddd, J 12, 11, 8, H-8), 1.72 (ddd, J 16, 7, 1, H-5e'), 1.86 (dd, J 12, 8, H-8), 1.97 (dqm, J 7, 7, H-6e), 2.07 (dddm, J 16, 7, 2, H-5a'), 2.22 (ddqd, J 10, 8, 6.5, 4, H-10), 2.30 (qqm, J 7, 7, H-11), 4.94 (ddm, J 7, 2 H-4). ^{13}C NMR (100.61 MHz, $CDCl_3$) δ: 37.7 (d, C-1), 16.9 (d, C-2), 145.6 (s, C-3), 110.2 (d, C-4), 30.9 (t, C-5), 27.3 (d, C-6), 37.4 (s, C-7), 32.2 (t, C-8), 29.8 (t, C-9), 35.3 (d, C-10), 35.7 (d, C-11), 21.9 (q, C-12), 21.2 (q, C-13), 18.6 (q, C-14), 18.0 (q, C-15).

4. Analytical data for **5**: $[\alpha]^{20}_{580}$ -199.7° (c 6.01, $CHCl_3$); HRMS m/e for $C_{15}H_{24}$: calcd. 204.1878, obsd. 204.1878. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 1.032 (d, J 6.5, CH_3-14), 1.034 (d, J 6.5, CH_3-15), 1.04 (d, J 2.5, H-2), 1.06 and 1.08 (d, J 7, CH_3-12 and CH_3-13), 0.91 (dddd, J 13, 11, 10, 8, H-9), 1.22 (dd, J 4, 3, H-1), 1.44 (ddddd, J 16, 11, 2, 2, 1, H-5a'), 1.56 (dd, J 12, 8, H-8), 1.64 (ddd, J 13, 8, 8, H-9), 1.77 (dqd, J 11, 6.5, 6, H-6a), 2.01 (ddd, J 16, 6.5, 6, H-5e'), 2.02 (ddd, J 12, 11, 8, H-8), 2.21 (ddqd, J 10, 8, 6.5, 4, H-10), 2.31 (qqm, J 7, 7, H-11), 5.09 (dddd, J 6.5, 2, 1, 1, H-4). ^{13}C NMR (100.61 MHz, $CDCl_3$) δ: 35.1 (d, C-1), 18.6 (d, C-2), 145.4 (s, C-3), 113.0 (d, C-4), 32.2 (t, C-5), 25.9 (d, C-6), 36.6 (s, C-7), 30.0 (t, C-8), 29.4 (t, C-9), 35.63 (d, C-10), 35.61 (d, C-11), 22.1 (q, C-12), 21.1 (q, C-13), 19.2 (q, C-14), 18.1 (q, C-15).

5. Analytical data for **7**: $[\alpha]^{20}_{580}$ -2.9° (c 6.80, $CHCl_3$); HRMS m/e for $C_{15}H_{24}$: calcd. 204.1878, obsd. 204.1880. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 0.70 (d, J 6.5, CH_3-15), 1.03 and 1.12 (s, CH_3-12 and CH_3-13), 1.12 (dddd, J 13, 13, 11, 6, H-9a), 1.24 (d, J 11, H-11), 1.42 (dddd, J 13, 13, 6, 3, H-10a), 1.48 (ddd, J 4, 3, 3, H-1), 1.59 (ddd, J 13, 6, 6, H-9e), 1.65 (dqd, J 11, 6.5, 6, H-8a), 1.68 (dddd, J 13, 6, 3, 2.5, H-10e), 1.74 (m, CH_3-14), 1.82 (dm, J 15, H-6), 1.85 (ddd, J 11, 4, 2.5, H-11), 2.26 (dm, J 15, H-6), 2.28 (br.s, H-3), 5.16 (m, H-5). ^{13}C NMR (100.61 MHz, $CDCl_3$) δ: 49.1 (d, C-1), 42.6 (s, C-2), 61.7 (d, C-3), 140.7 (s, C-4), 124.7 (d, C-5), 39.0 (t, C-6), 55.8 (s, C-7), 38.1 (d, C-8), 30.4 (t, C-9), 28.5 (t, C-10), 46.5 (t, C-11), 25.2 (q, C-12), 26.6 (q, C-13), 17.2 (q, C-14), 17.1 (q, C-15).

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