Letters to the Editor

Isomerization of 5-(cyclopentadienylidenemethyl)bicyclo[2.2.1]hept-2-ene catalyzed by Al_2O_3

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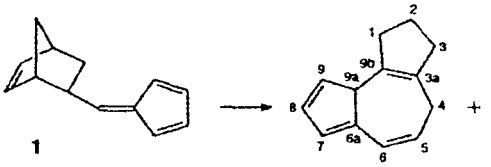
Earlier,[1,2] it was shown that thermolysis of 5-(cyclopentadienylidenemethyl)bicyclo[2.2.1]hept-2-ene (**1**) at 500—520 °C yields 1,2- and 1,5-dihydropentalenes, the reaction proceeding *via* intermediate 6-vinylpentafulvene.



In the present work, it was found for the first time that compound **1** transforms into a mixture of 2,3,4,9a-tetrahydro- (**2**), 2,3,4,9-tetrahydro- (**3**), and 2,3-dihydro-1*H*-cyclopenta[*e*]azulene (**4**) in the presence of Al_2O_3 under gas-phase conditions at 400 °C and 3 Torr (overall yield 48%, the ratio 1.1 : 1.8 : 1, respectively). This opens an unexpectedly simple route to 2,3-dihydro-1*H*-cyclopenta[*e*]azulene derivatives.[3—6] Note that compound **4** is a product of dehydrogenation of **2** and/or **3**.

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13 and 75.47 MHz, respectively) in $CDCl_3$.

Isomerization of 1. Compound **1** (0.77 g, *endo* : *exo* = 4 : 1) in gas phase was passed at 400 °C and 3 Torr through a quartz reactor (l = 45 cm, d = 1 cm) filled with Al_2O_3. The reaction products were condensed at −196 °C and chromatographed on a column with silica gel L 100/160 μm (pentane was used as the eluent) to give a mixture of previously unknown regioisomers **2** and **3** (total yield 0.26 g, 33.8%) in the ratio 1 : 3 (^1H NMR) as a yellowish oil and product **4** (0.11 g, 14.3%) as a blue violet oil. The ratio of isomers **2** and **3** changes during column chromatography because of their isomerization on SiO_2.

2,3,4,9a-Tetrahydro-1*H*-cyclopenta[*e*]azulene (2). ^1H NMR ($CDCl_3$), δ: 2.22 (quint, 2 H, CH_2, J = 7.5 Hz); 2.41 (s, 2 H, CH_2); 2.87 (t, 2 H, CH_2, J = 7.5 Hz); 2.98 (t, 2 H, CH_2, J = 7.5 Hz); 3.36 (d, 1 H, CH, J = 5.0 Hz); 6.53—6.61 (m, 3 H, CH); 6.92—7.17 (m, 2 H, CH). ^{13}C NMR ($CDCl_3$), δ: 19.28; 24.65; 25.83; 31.11; 32.70; 119.94; 121.38; 123.43; 130.03; 130.59; 131.51; 131.78; 133.14. MS, m/z: 170 $[M]^+$. Found (%): C, 91.63; H, 8.32. $C_{13}H_{14}$. Calculated (%): C, 91.71; H, 8.29.

2,3,4,9-Tetrahydro-1*H*-cyclopenta[*e*]azulene (3). ^1H NMR ($CDCl_3$), δ: 2.25 (quint, 2 H, CH_2, J = 7.5 Hz); 2.33 (s, 2 H, CH_2); 2.85 (t, 2 H, CH_2); 2.91 (t, 2 H, CH_2, J = 7.5 Hz); 3.07 (t, 2 H, CH_2, J = 7.5 Hz); 6.54—6.66 (m, 2 H, CH); 6.94—7.14 (m, 2 H, CH). ^{13}C NMR ($CDCl_3$), δ: 19.48; 25.02;

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25.63; 31.53; 32.77; 121.81; 122.59; 122.99; 130.36; 130.74; 132.21; 132.30; 133.49. MS, *m/z*: 170 $[M]^+$. Found (%): C, 91.63; H, 8.32. $C_{13}H_{14}$. Calculated (%): C, 91.71; H, 8.29.

2,3-Dihydro-1*H*-cyclopenta[*e*]azulene (4). ^{1}H NMR ($CDCl_3$), δ: 2.23 (quint, 2 H, CH_2, J = 7.5 Hz); 3.29 (t, 2 H, CH_2, J = 7.3 Hz); 3.57 (t, 2 H, CH_2, J = 7.6 Hz); 7.11 (t, 1 H, CH, J = 9.8 Hz); 7.25 (d, 1 H, CH, J = 3.6 Hz); 7.31 (d, 1 H, CH, J = 3.7 Hz); 7.67 (d, 1 H, CH, J = 9.9 Hz); 7.85 (t, 1 H, CH, J = 3.8 Hz); 8.30 (d, 1 H, CH, J = 9.6). ^{13}C NMR ($CDCl_3$), δ: 24.65; 37.04; 38.17; 114.13; 117.21; 121.40; 133.50; 134.70; 134.95; 136.17; 139.32; 140.36; 152.26. MS, *m/z*: 168 $[M]^+$. The compound obtained is spectrally identical with the known one.[6]

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Electronic properties and chemical composition of wurtzite-like SiAlON polytypes

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Polytype formation is known for many various crystalline compounds.[1] Modern schemes of polytype classification and many models of polytype formation are based on the principles of their structural state and structural conformity.[2] Assume that the formation of the so-called concentration polytypes of a certain system is defined by the unified nature of their electron-energy states (EES), then the quantum-chemical simulation of the chemical composition of the polytypes can be performed, and their existence can be explained from the viewpoint of the band theory of crystals and chemical bond theory. The results obtained correspond to the experimental data on compositions of the known polytypes.

Let us illustrate the approach proposed by the wurtzite-like polytypes in the Si—Al—O—N system (so-called sialones[3]). These polytypes are developed from AlN during dissolution of Si and O to form a family of multilayered structures with the common composition $Al_{x+y}Si_{6-x}O_xN_{8-x}$ (x = 4; y = 2n, n is an integer), which are built from "blocks" with different chemical compositions, (AlN) and ($AlNSiO_2$), and each polytype can be presented as m(AlN)($AlNSiO_2$), where m is an integer.

Let us consider EES of the basis AlN phase. The total density of the states and overlapping populations of crystalline orbitals (OPCO is the band analog of overlapping populations that are well-known in quantum chemistry of molecules) obtained by the band calculation of AlN using the 32-atomic super cell are presented in Fig. 1. The valent band (VB) is filled and separated from the unoccupied conductivity band (CB) by a broad forbidden gap (FG 7.4 eV). The OPCOs in VB are positive and those in CB are negative. Therefore, the optimum condition of chemical stability of a crystal is fulfilled for AlN: all bonding states are occupied, and antibonding states are vacant.

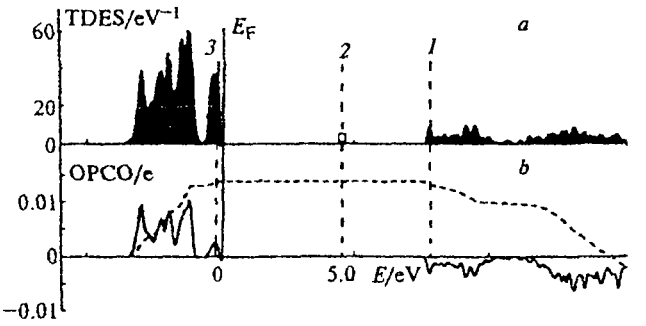

Fig. 1. Total density of electron states (TDES) (*a*) and overlapping populations of crystalline orbitals (OPCO) (*b*) for AlN. Dotted lines indicate the position of the Fermi level (E_F) for the AlN + O (*1*), AlN + Si (*2*), and AlN + V_{Al} (*3*) systems. For AlN + Si, the energy position of new doped bands is marked with the square. The Fermi levels of the 13AlN($AlNSiO_2$) polytype and AlN (solid line) coincide. The band calculations were performed using 32-atomic supercells.

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