The mass spectrum (EI) of compound **3** contains a molecular ion peak with m/z = 183 (100 %). Its ^{1}H NMR spectrum contains two doublets of aromatic H(2) (δ 8.08) and H(4) (δ 7.07, $J_{2,4}$ = 2.1 Hz) protons along with two singlets at δ 3.74 and 3.51, which were assigned to MeO and MeN protons, respectively. More detailed information on the structure of compound **3** is obtained from the ^{13}C NMR spectrum, where the line assignments were based on the chemical shifts[6,7] and $J_{C,H}$[8] values for related compounds. The MeN signal is observed at δ 38.20. In this case the quartet components (^1J = 141.6 Hz) are additionally split into doublets due to interaction with the H(2) proton (^3J = 3.7 Hz). MeO gives a quartet with δ 56.61 (^1J = 145.3 Hz). A MeO group in position 5 is characterized by the quartet splitting of the doublet components of the C(5) signal registered at δ 148.89 as a quintet because of equal ^3J and ^2J constants (3.7 Hz). The protons of the MeN group cause additional quartet splitting of the doublet-doublet components of the C(2) signal (δ 136.72, ^3J = 3.7 Hz); the doublet components (^1J = 187.8 Hz) manifest themselves as quintets because of equal ^3J constants (3.7 Hz).

Experimental

The mass spectrum (EI, 70 eV) was recorded on an MKh-1321A spectrometer by the direct inlet of the sample into the ionization chamber of the evaporator (100 °C). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WH-90 (90 MHz and 22.62 MHz, respectively) spectrometer in DMSO-d_6 at 40 °C. Concentrations of substances in solutions were 2 % and 10 %, respectively. Chemical shifts (δ) were measured relative to $SiMe_4$ (^{1}H) and ane (^{13}C).

1-Methyl-5-methoxy-6-oxo-1,6-dihydro-3-pyridine carboxylic acid (3). Me_2SO_4 (2 g, 15.9 mmol) was added portionwise to a solution of acid **1** (0.5 g, 3.2 mmol) in 10% aqueous NaOH (5 mL). The mixture was stirred for 3 h at ~20 °C, the excess Me_2SO_4 was extracted with ether, and the water layer was neutralized with dilute H_2SO_4 to pH 4. The precipitate that formed upon cooling was filtered off, dried, and recrystallized from water with the addition of carbon. Compound **3** (0.23 g, 39 %) was obtained; m.p. 257—258 °C. Found (%): C, 52.61; H, 4.95; N, 7.72. $C_8H_9NO_4$. Calculated (%): C, 52.50; H, 4.91; N, 7.65.

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Formation of azulene and naphthalene from piperylene

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Piperylene mixed with air is converted into a mixture of aromatics containing azulene and naphthalene on contact with bismuth oxide at ~600 °C. The yield of azulene and naphthalene is 6—8 %. The reaction is accompanied by burning of some of the piperylene and by the reduction of Bi_2O_3 to Bi metal. When the initial mixture is diluted with steam no reduction occurs. The reaction is believed to involve elimination of the allylic hydrogen, formation of dienyl radicals, their dimerization, and subsequent aromatization.

Key words: azulene, naphthalene, piperylene, dehydrodimerization.

It has been reported previously[1] that in the presence of some dehydrogenation catalysts, piperylene is converted into azulene (0.2—0.5 %) and naphthalene (0.3—0.7 %). Since the yields of these products from 1-decene are markedly higher, we suggested that the transformation of piperylene into them occurs *via* a linear interme-

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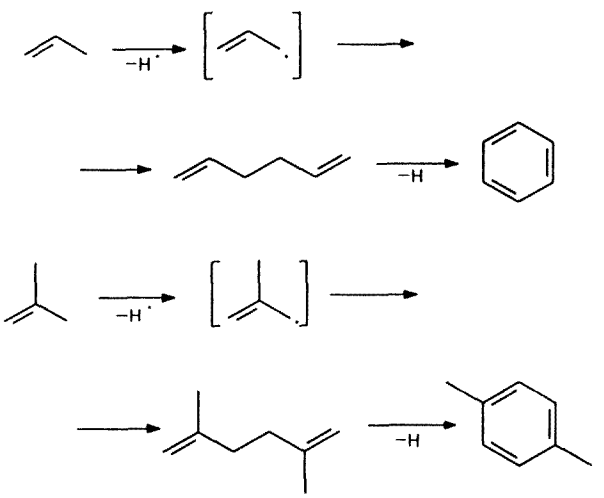
Scheme 1



diate of the composition C_{10}. If this is true, one should expect that the yields of azulene and naphthalene would substantially increase in the presence of catalysts with pronounced dehydrodimerizing activity. One of these catalysts is Bi_2O_3; its compositions with other oxides, in particular, with SnO_2, can also be used. Under conditions of oxidative dehydrogenation, these catalysts convert low-molecular-weight olefins into dimeric dienes, and under more rigorous conditions, olefins are converted into aromatic hydrocarbons.[2–5] According to the data reported previously,[6–10] the reaction involves abstraction of the allylic hydrogen to give allyl radicals and their subsequent dimerization (Scheme 1).

We suggested that the use of Bi_2O_3-containing catalysts in the transformation of piperylene should be favorable for the formation of dehydrodimers, and then for their conversion into the corresponding fused aromatic hydrocarbons (Scheme 2).

It was found that when piperylene mixed with air is passed over Bi_2O_3 at temperatures of ~600 °C, an intensely blue-colored liquid products is formed. The liquid products contains 6.1 % azulene and 37.7 % naphthalene; unreacted piperylene, cyclopentene, cyclopentadiene, and mononuclear C_6—C_{10} aromatic

Scheme 2

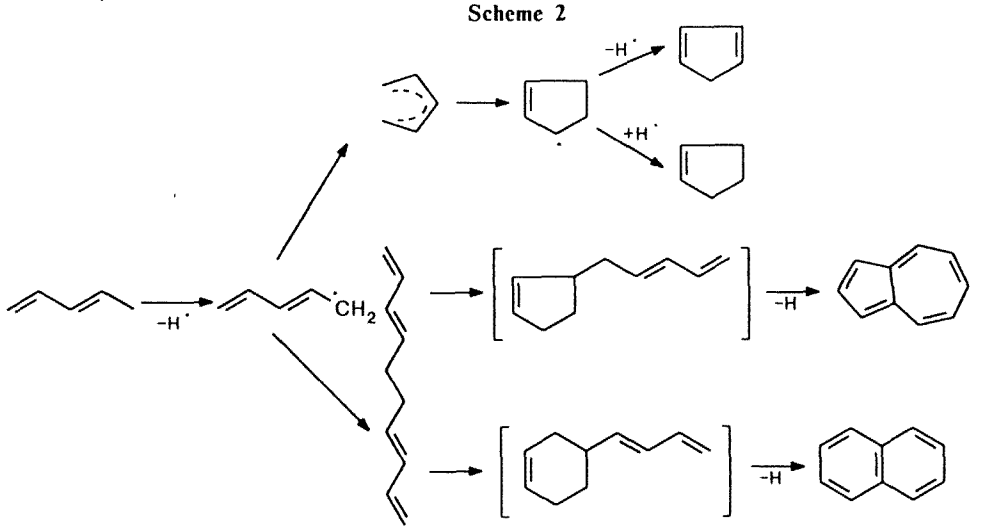


Table 1. Formation of azulene and naphthalene in the presence of bismuth oxide at 600 °C

Run	Residence time of SGM /s[a]	C_5H_8:O_2: :N_2:H_2O ratio	Yield of liquid (%)	Proportions in the catalyzate (%)								Yield (%)	
				n-C_5H_8	Cyclopentene+ cyclopentadiene	Benzene	Toluene	Arenes C_8	Arenes C_9—C_{10}	Naphthalene	Azulene	Naphthalene	Azulene
1	4.7	1:1.2:4.7:—	18.0	10.5	2.0	14.4	4.8	8.4	7.4	37.8	6.1	6.8	1.1
2	2.8	1:0.7:8.9:—	30.0	83.5	2.5	3.5	0.7	0.6	0.7	2.4	0.5	0.7	0.2
3	1.0	1:1.4:5.33:—	57.4	91.7	1.0	1.9	0.4	0.6	0.6	0.8	0.2	0.5	0.1
4	4.7	1:2.1:8.4:—	Flash of SGM										
5	1.8	1:0.45:1.8:6	70.0	69.4	1.8	9.4	1.2	1.8	0.5	5.7	2.5	4.0	1.8
6	2.5	1:0.45:1.8:6	47.8	71.7	2.3	6.3	1.3	2.0	3.1	7.5	2.3	3.6	1.1
7[b]	1.8	1:0.45:1.7:6	68.2	87.4	1.0	3.5	0.4	0.4	Traces	0.8	0.5	0.6	0.4
8[c]	1.8	1:0.45:1.8:6	82.6	85.9	0.2	1.1	0.1	0.1	Traces	0.2	0.1	0.2	0.1

[a] Steam-gas mixture. [b] At 550 °C. [c] At 500 °C.

Table 2. Formation of azulene and naphthalene in the presence of mixed Bi_2O_3-containing catalysts at 600 °C

Catalyst	Residence time /s	C_5H_8:O_2:H_2:H_2O ratio mol.	Yield of liquid (%)	Yield (%)	
				Naphthalene	Azulene
20 % Bi_2O_3—SiO_2	4.7	1:1.2:4.7:—	65.8	0.1	—
	4.0	1:0.7:2.5:3.7	90.5	0.1	—
40 % Bi_2O_3—MgO	4.7	1:1.2:4.7:—	46.5	0.1	0.1
	4.0	1:0.7:2.5:3.7	41.4	0.2	0.1
SnO_2	1.8	1:0.45:1.8:6	57.7	0.3	Traces
25 % Bi_2O_3—SnO_2	1.8	1:0.45:1.8:6	41.7	0.4	0.1
50 % Bi_2O_3—SnO_2	1.8	1:0.45:1.8:6	31.1	1.3	0.1
75 % Bi_2O_3—SnO_2	1.8	1:0.45:1.8:6	46.0	2.7	0.3
Bi_2O_3	1.8	1:0.45:1.8:6	47.8	3.8	1.1

hydrocarbons were also detected in it. Since the overall yield of the liquid products is rather low (16 %), the yields of azulene and naphthalene are only 1.1 and 6.8 %, respectively. The low yield of the liquid products is due to burning of some of the initial hydrocarbon. Therefore, the amount of liquid products decreases as the proportion of oxygen in the initial mixture increases or as the residence time increases (Table 1, runs *1*—*4*). When the dilution with air is too high (run *4*), the reaction mixture explodes; while at low dilutions (run *1*), Bi_2O_3 is partly reduced to metallic bismuth. The use of steam as the diluent makes it possible to avoid the reduction of Bi_2O_3 even at low proportions of air in the reaction mixture. Simultaneously, the yield of the liquid products increases to 50—70 %, and the overall yield of azulene and naphthalene is 5.8 %. As the reaction temperature decreases, the latter dramatically decreases, and the proportion of azulene simultaneously increases (see Table 1, runs *5*, *7*, and *8*). In the presence of mixed bismuth catalysts containing MgO, SiO_2, or SnO_2, which have been studied previously in the dehydrodimerization of lower olefins, the yield of fused arenes from piperylene decreased, and the proportion of azulene in them was lower than with the individual Bi_2O_3 (Table 2).

Thus, the yields of azulene and naphthalene from piperylene in the presence of Bi_2O_3 is almost an order of magnitude higher than that observed previously over dehydrogenation catalysts.[1] The efficiency of bismuth oxide in this reaction is indirect evidence supporting the concept of the abstraction of the H-atom from the allylic position of the piperylene molecule to give a pentadienyl radical, which then undergoes dimerization and aromatization (see Scheme 2). The formation of C_5 cyclic hydrocarbons, cyclopentene and cyclopentadiene is also consistent with this concept. However, in our case, the pentadienyl radical is probably not dimerized, and, instead, undergoes immediate cyclization to give a cyclopentenyl radical, which is stabilized by adding or eliminating a hydrogen atom. The relatively high content of benzene and its homologs in the liquid products can be explained by cracking of the dehydrodimer to yield polyunsaturated hydrocarbons with fewer carbon atoms.

Experimental

The experiments were carried out in a flow-type setup with a vertical quartz reactor placed in a block electric furnace. Piperylene was introduced using a dosing injector, and the reaction products were collected in cooled coil traps. Simultaneously, air was introduced into the reaction area at a rate controlled by a flowmeter, and in some cases, steam was also introduced as an additional diluent. The conditions of the experiments are presented in Tables 1 and 2.

The reaction products were analyzed by GLC using a 40 m×0.25 mm stainless-steel column wetted by Apiezon N. The analysis was carried out at 130 °C, which allowed azulene and naphthalene to be eluted, along with mononuclear arenes. Azulene and naphthalene were also isolated by preparative chromatography of the reaction mixture on a column with Al_2O_3 (using isopentane as the eluent). Both isolated products were identified by their UV spectra.

Bi_2O_3 was obtained from $Bi(NO_3)_3 \cdot 5H_2O$ dissolved in concentrated HNO_3. $Bi(OH)_3$ was precipitated from this solution by adding a 15 % solution of NH_4OH (to pH 3). The precipitate was washed with distilled water on a filter, dried at 150 °C, and calcined in a muffle furnace for 6 h at 550 °C. Bi_2O_3—MgO was prepared by wet mixing of MgO and Bi_2O_3 powders (the fraction less than 63 mm in size) followed by drying and calcination, as described above. The Bi_2O_3—SnO_2 catalysts were obtained by precipitating $Bi(OH)_3$ in the presence of an SnO_2 powder, prepared by dissolution of metallic tin in concentrated HNO_3, according to a known procedure.[12] The mixed $Bi(OH)_3$—SnO_2 precipitate was centrifuged, and then, after washing with distilled water and repeated centrifugation, it was dried and calcined as described above. Bismuth-containing precipitates caked during the calcination to give a solid material, which was then milled, and the 1—2 mm fraction was picked up. The Bi_2O_3—SiO_2 samples were prepared by impregnation of SiO_2 grains (1—2 mm) with a solution of $Bi(NO_3)_3 \cdot 5H_2O$ in HNO_3 followed by evaporation, drying, and calcination as described above.

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Analysis of chiroptical properties of π-allyl complex [Pd(β-pinenyl)Cl]$_2$

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Electronic absorption and circular dichroism spectra of the optically active [Pd(β-pinenyl)Cl]$_2$ complex (**1**) have been studied. The assignment of the bands in the circular dichroism spectrum in the d—d-transition region of complex **1** was made within the framework of the one-electron model of optical activity; this assignment is in agreement with the literature data on the analysis of the absorption spectrum of [Pd(allyl)Cl]$_2$. The (1*R*,2*S*,3*S*,5*R*) absolute configuration was suggested for the optical $(+)_{589}$-isomer of **1** studied.

Key words: chirality, absolute configuration; circular dichroism; electronic absorption spectra; Pd(π-allyl) complexes.

π-Allyl complexes of Pd[II] are widely used in synthesis and catalysis, including their asymmetrical variations.[1,2] However, studies of the relationship between the stereochemistry and the optical activity of complexes, which were started as early as 1970s[3] and which are necessary for performing stereospecific conversions, are not yet widespread. The precise assignment of transitions in the electronic absorption and circular dichroism spectra of compounds is necessary for revealing these correlations. Analysis of electronic absorption and circular dichroism spectra of organometallic compounds may substantially help in the study of the nature of chemical bonds and characteristic features of the structures, which cannot be currently calculated by quantum-chemical methods.

Electron transitions are generally more pronounced in the circular dichroism spectra. Therefore, we use the circular dichroism method for studying chiral π-allyl complex [Pd(β-pinenyl)Cl)]$_2$ (**1**). Analysis of the circular dichroism spectrum was carried out within the framework of the one-electron model of optical activity.[4,5] To our knowledge, such analysis of π-allyl complexes has not been previously performed. Interest in chiroptical properties of complex **1** is also associated with the use of this complex in the synthesis of the new chiral [Fe_3CoCPd(β-pinenyl)$(CO)_{12}$] cluster.[6]

Complex **1** was prepared by the reaction of Na_2PdCl_4 with β-pinene ($[\alpha]_D$ −19.7°) using the known procedure.[7] The compound obtained is characterized by a

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