cell. The recording of CL upon the isomerization of DMD absorbed from the gas phase on the sorbent surface was carried out analogously, placing Silipor (50 mg, Silipor 400, Chemapol, 0.125—0.160 mm, 400 $m^2 g^{-1}$) in the second cell. The phosphorescence spectrum of $^3MA^*$ (λ_{max} = 390 nm) was recorded on a Hitachi MPF-4 spectrofluorimeter at 77 K.

Results and Discussion

The intensity of CL observed upon the decomposition of DMD in the gas phase (90 °C) is equal to $\approx 5 \cdot 10^5$ photon s^{-1} mL^{-1} per angle of 4π. The spectral composition of this luminescence, estimated with the aid of light filters, corresponds to the phosphorescence spectrum of $^3MA^*$. The CL intensity increases as temperature increases and decreases when the argon supply is stopped.

A much more bright CL (more than 10 times) was recorded upon the isomerization of DMD absorbed from the gas phase on the Silipor surface. The emission efficiency of triplet molecules on the sorbent surface is known to increase;[4] the rate of chemical transformation of labile molecules (such as 1,2-dioxethanes) also increases.[5] It is likely that the isomerization of DMD and favorable conditions for phosphorescence of $^3MA^*$ on the silipor surface result in increasing the CL intensity. If the argon flow through the cell is constant, the intensity of CL rapidly increases and then decreases following the exponential law. This behavior of CL is most likely associated with the establishment of the adsorption-desorption equilibrium of DMD and MA and a decrease in the activity of the adsorption centers. When the argon flow is stopped, CL drops more rapidly, which is due to isomerization of the adsorbed DMD. In the successive cycles of switching on—switching off the argon supply changes in the luminescence are repeated. It should be noted that the effective rate constant of quenching of CL for adsorbed DMD (k_{eff} = $(1.1 \pm 0.1) \cdot 10^{-2}$ s^{-1}) at 90 °C is nearly an order of magnitude lower than the rate constant of the decomposition of DMD in solution, obtained by the extrapolation of the Arrhenius dependence to T = 90 °C (k_{sol} = 0.13 s^{-1}). A decrease in the rate of decomposition of DMD adsorbed from the gas phase on the Silipor surface apparently is associated with the absence of processes (interaction with the solvent, catalysis by impurities, the chain decomposition, *etc.*) favoring the transformation of DMD in solution.

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On the [4+2]-cycloaddition reaction of levoglucosenone with piperylene

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The Diels—Alder reaction of levoglucosenone with piperylene catalyzed by $ZnCl_2$ proceeds regio- and stereoselectively to give the *sin—cis*-adduct **3**; the thermal reaction yields an epimeric mixture of compound **3** with *sin—trans*-adduct **4** in the ratio of 4 : 1.

Key words: levoglucosenone, piperylene, cycloaddition, regio- and stereoselectivity.

Alicyclic 1,3-dienes of different types: butadiene, 1-acetoxy- and 1-trimethylsiloxybutadienes, and 1-benzyloxymethyl-3-methoxybutadiene, readily enter the thermal Diels—Alder reaction with levoglucosenone (**1**)[1,2] to yield the corresponding [4+2]-cycloadducts of type **2**.[3—6] The reactions proceed according to an unam-

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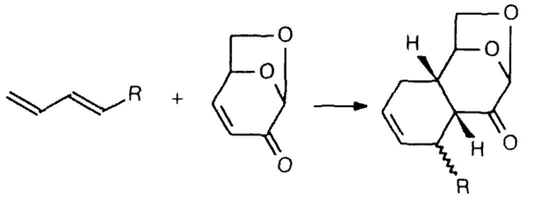
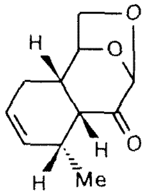
biguous regiochemical pattern and endo-"stereospecifically";[7] however, the cycloaddition process as a whole is not completely stereoselective: compounds **2** form, which are epimeric at the centers bearing the substituent R.

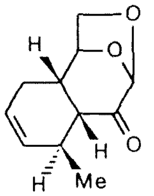


1 **2**

Earlier we reported the highly regio- and stereoselective Diels—Alder reaction of levoglucosenone with isoprene catalysed by $ZnCl_2$.[8] We continued this research and studied the reaction of compound **1** with piperylene under the same conditions as for isoprene in order to obtain novel vicinal functionalized methyl-containing cyclohexenes with correct configuration of chiral centers. Such systems are of interest as starting synthons in enantiospecific approaches to a number of natural products. It has been found that piperylene reacts with compound **1** (20 °C, 12 h) in a CH_2Cl_2 solution containing a catalytic amount of anhydrous $ZnCl_2$ to give pure adduct **3** in an 85% yield. At the same time, the thermal reaction of piperylene with levoglucosenone is not stereoselective; it gives adducts **3** and **4** in a ratio of 4 : 1 (^1H NMR).



3



4

For assignment of epimeric methylcyclohexenes **3** and **4**, the ^1H NMR data are characteristic. The pyranose ring of compounds **3** and **4**, as for other 1,6-hexapyranose derivatives[9], is locked in the $^1C_4$-conformation, and the cyclohexene rings linked with it are in the boat conformation with the C=C moiety being *exo*-oriented.[3] When the system of fused rings is arranged in such a manner, the molecular models indicate that the equatorially oriented methyl group in α-isomer **3** is affected by anisotropic shifting effect of the carbonyl group as a result of proximal relative position and convergence [10] and its resonance signal is markedly shifted downfield in comparison with the signal from the Me-group of the β-isomer. We also observed significant differences in CSSI of C(7)H-epimers. Thus, the signal from C(7)H of epimer **4** is a doublet with $J_{7,2} = 6.3$ Hz ($J_{7,6}$ ~0!, *cf.* Ref. 3), whereas C(7)H of epimer **3** resonates as doublets with $J_{7,2} = 5.4$ and $J_{7,6} = 5.3$ Hz.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300 and 75.47 MHz, respectively) in $CDCl_3$ with TMS used as an internal standard. TLC was carried out on chromatographic Silufol plates (Czechia). Rotation angles were measured on a Perkin—Elmer instrument.

Diels-Alder reaction of levoglucosenone with piperylene. *A*. Catalytic method. Crystals of anhydrous $ZnCl_2$ (0.05 g, 0.37 mmol) were added to a solution of levoglucosenone (0.5 g, 3.9 mmol) and piperylene (0.5 g, 7.3 mmol) in 20 mL of CH_2Cl_2, with stirring, and the resulting mixture was then stirred at 20 °C for 12 h. The reaction mixture was washed with water and a saturated solution of NaCl, dried over $MgSO_4$, and evaporated; the resulting residue was crystallized from a petroleum ether—diethyl ether solution (7 : 3) to yield compound **3** (0.64 g, 85%).

(1*S*, 2*S*, 6*R*, 7*R*, 9*R*)-10,12-Dioxatricyclo[7.4.2.1.$0^{2,7}$]-6-methyl-4-dodecen-8-one (3). R_f 0.24 (ethyl acetate—heptane, 3 : 7). M.p. 128—129 °C. $[\alpha]^{20}_D$ 69.3° (1.0, $CHCl_3$). ^1H NMR, δ: 1.29 (d, 3 H, CH_3, $J = 7.5$ Hz); 2.05—2.18 (*m*, 1 H, CH); 2.32—2.63 (m, 3 H, CH_2, CH); 3.20 (dd, 1 H, C(7)H, $J_{7,2} = 5.4$, $J_{7,6} = 5.3$ Hz); 4.03 (dd, 1 H, C(11)H, $J_{11,1} = 4.9$, $J_{11,11'} = 7.4$ Hz); 4.21 (d, 1 H, C(11')H, $J_{11',11} = 7.4$ Hz); 4.42 (m, 1 H, C(2)H); 5.10 (s, 1 H, C(9)H); 5.60 (br.s, CH=CH).

^{13}C NMR, δ: 17.77 (CH_3); 24.38 (C(3)); 30.60 (C(6)); 43.83 (C(2)); 44.17 (C(7)); 67.45 (C(11)); 77.06 (C(1)); 102.66 (C(9)); 124.13 (C(4)); 130.62 (C(5)); 203.35 (C(8)).

Mass spectrum (EI), *m/z* (I_{rel} (%)): 194 $[M]^+$ (23), 193 $[M-H]^+$ (11), 168 $[M-C_2H_2]^+$ (5), 148 $[M-CO-H_2O]^+$(61), 130 $[M-CHO-OH-H_2O]^+$ (30), 120 $[M-C_3H_6O_2]^+$ (53). Found (%): C, 67.16; H, 7.39. $C_{11}H_{14}O_3$. Calculated (%): C, 68.01; H, 7.28.

***B*. Thermal method.** A solution of levoglucosenone (0.5 g, 3.9 mmol) and piperylene (0.6 g, 9.0 mmol) in 6 mL of toluene was heated in a sealed glass tube (Pyrex) for 5 h at 160 °C). The tube was opened, the solvent was distilled off on a rotary evaporator, and the residue was chromatographed on silica gel using an ethyl acetate—petroleum mixture (1 : 9) as the eluent. A mixture of isomeric products **3** and **4** in a ratio 4 : 1 (0.61 g, 81%) was obtained.

(1*S*, 2*S*, 6*R*, 7*S*, 9*R*)-10,12-Dioxatricyclo[7.4.2.1.$0^{2,7}$]-6-methyl-4-dodecen-8-one (4). ^1H NMR, δ: (from the mixture with adduct **3**): 0.99 (d, 3 H, CH_3, $J = 7.3$ Hz); 1.95—2.50 (*m*, 3 H, CH_2, CH); 2.78 (d, 1 H, C(7)H, $J_{7,2} = 6.3$ Hz) 3.92 (m, 1 H, C(11)H); 4.12 (d, 1 H, C(11')H, $J_{11',11} = 7.9$ Hz); 4.42 (d, 1 H, C(1)H, $J = 4.3$ Hz); 5.02 (s, 1 H, C(8)H); 5.50 (m, 2 H, CH=CH).

^{13}C NMR, δ: 21.47 (CH_3); 24.16 (C(3)); 24.87 (C(6)); 37.85 (C(2)); 45.30 (C(7)); 67.18 (C(11)); 77.27 (C(1)); 101.46 (C(9)); 123.38 (C(4)); 130.07 (C(5)); 202.16 (C(8)).

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Schemes of calculation of the properties of substituted ethylenes

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Calculation schemes for estimation of the properties of X-substituted ethylenes based on the concept of atoms interacting in pairs are described. The equivalence of these schemes are shown, and the relations between their parameters are established.

Key words: schemes of additivity; interactions of atoms, substituted ethylenes.

Several schemes of calculation occur in the literature for X-substituted ethylenes (X = Cl, Me, ...), which present a certain property as the sum of properties (P) due to interactions of atoms in pairs, valence interactions (p_{CC_0}, p_{CH_0},...), nonvalence interactions of alternate atoms (p_{CH_1}, p_{HH_1},...), and nonvalence interactions of every third alternate atoms (p_{HH_2},...), taking into account their *cis*- (0) or *trans*- (π) positions:

1) Bernstein's scheme[1]

$$P_{CH_{2-l}X_l=CH_{2-l'}X_{l'}} = P_0 + x_a a + x_b b + x_c c + x_d d, \qquad (1)$$

where

$$\left.\begin{aligned} P_0 &= p_{CC_0} + 4p_{CH_0} + 4p_{CH_1} + 2p_{HH_1} + 2p^0_{HH_2} + \\ &\quad + 2p^\pi_{HH_2}, \\ a &= -p_{CH_0} + p_{CX_0} - p_{CH_1} + p_{CX_1} - p_{HH_1} + p_{HX_1} - \\ &\quad - p^0_{HH_2} - p^\pi_{HH_2} + p^0_{HX_2} - p^\pi_{HX_2}, \\ b &= -p_{CH_0} + p_{CX_0} - p_{CH_1} + p_{CX_1} - p_{HX_1} + p_{XX_1} - \\ &\quad - p^0_{HH_2} - p^\pi_{HH_2} + p^0_{HX_2} - p^\pi_{HX_2}, \\ c &= -p_{CH_0} + p_{CX_0} - p_{CH_1} + p_{CX_1} - p_{HH_1} + p_{HX_1} - \\ &\quad - p^0_{HH_2} - p^0_{HX_2} - p^\pi_{HX_2} + p^\pi_{XX_2}, \\ d &= -p_{CH_0} + p_{CX_0} - p_{CH_1} + p_{CX_1} - p_{HH_1} + p_{HX_1} - \\ &\quad - p^\pi_{HH_2} - p^0_{HX_2} + p^\pi_{HX_2} + p^0_{XX_2} \end{aligned}\right\} \qquad (2)$$

2) the scheme proposed in Ref. 2

$$P_{CH_{2-l}X_l=CH_{2-l'}X_{l'}} = \lambda_0 + (l + l')\lambda_1 + (l^2 + l'^2)\lambda_2 + \\ + (ll')\lambda_3 \pm q^{HX}, \qquad (3)$$

where

$$\left.\begin{aligned} \lambda_0 &= p_{CC_0} + 4p_{CH_0} + 4p_{CH_1} + 2p_{HH_1} + 2p^0_{HH_2} + \\ &\quad + 2p^\pi_{HH_2}, \\ \lambda_1 &= -p_{CH_0} + p_{CX_0} - p_{CH_1} + p_{CX_1} - 3/2\, p_{HH_1} + \\ &\quad + 2p_{HX_1} - 1/2\, p_{XX_1} - p^0_{HH_2} - p^\pi_{HH_2} + p^0_{HX_2} + \\ &\quad + p^\pi_{HX_2}, \\ \lambda_2 &= 1/2\, p_{HH_1} - p_{HX_1} + 1/2\, p_{XX_1}, \\ \lambda_3 &= 1/2(p^0_{HH_2} + p^\pi_{HH_2} - 2p^0_{HX_2} - 2p^\pi_{HX_2} + p^0_{XX_2} + \\ &\quad + p^\pi_{XX_2}), \\ q^{HX} &= 1/2(p^0_{HH_2} - p^\pi_{HH_2} - 2p^0_{HX_2} + 2p^\pi_{HX_2} + \\ &\quad + p^0_{XX_2} - p^\pi_{XX_2}). \end{aligned}\right\} \qquad (4)$$

3) the scheme proposed by S. E. Tomberg[3]

$$P_{CH_{2-l}X_l=CH_{2-l'}X_{l'}} = \alpha_1[CH]_0 + \alpha_2[CX]_0 + \\ + \beta_1[HX]_1 + \beta_2[HX]^0_2 + \beta_3[HX]^\pi_2, \qquad (5)$$

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