## POLYFURYL(ARYL)ALKANES AND THEIR DERIVATIVES. 15.\* PRODUCTS FROM THE REDUCTION OF 2-NITROARYL-DIFURYLMETHANES. SYNTHESIS OF INDOLE DERIVATIVES

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The reduction of 2-nitrophenyldifurylmethane with  $SnCl_2$  leads to an indolenyl ketone as a result of intramolecular heterocycloaddition of the intermediately formed nitroso derivative. During the reduction of 2-nitroaryldifurylmethanes in the Zn + HCl or  $NH_2NH_2 \cdot H_2O + Pd/C$  systems, 2-aminoaryldifurylmethanes are formed; when treated with trityl perchlorate, their acetyl derivatives are converted into indolo[2,3-h]-1-oxazulenium perchlorates.

Aryldifurylmethanes are suitable precursors in the synthesis of heterocyclic systems. The deoxygenation of 2nitroaryldifurylmethanes leads to the formation of derivatives of carbazole [2,3]. We described the synthesis of derivatives of benzofuran [4, 5] from 2-hydroxyaryldifurylmethanes and also published a preliminary report on the synthesis of a derivative of indole [6]. In a continuation of our investigations into the use of *ortho*-substituted aryldifurylmethanes in the synthesis of heterocycles we studied the products from the reduction of 2-nitroaryldifurylmethanes and their transformations into indole derivatives.

As starting compounds we used the readily obtainable 2-nitroaryldifurylmethanes (Ia, b) [6, 7]. By their reduction with zinc dust in methanol in the presence of hydrochloric acid or trimethylsilyl chloride and also by the  $NH_2NH_2 \cdot H_2O + Pd/C$  system, we obtained fairly high yields of the corresponding anilines (IIa, b).



Different behavior is observed if  $SnCl_2 \cdot 2H_2O$  is used as reducing agent. Compound (Ib) is reduced to the aniline (IIb) as before, whereas compound (Ia) is converted into the unsaturated ketone (III) under these conditions. The structure of the product (III), proposed on the basis of the spectral data (the presence of bands at  $\nu = 3320$  and 1680 cm<sup>-1</sup> in the IR spectrum and signals for two olefinic protons in the region of 8.12 and 6.78 ppm with a spin-spin coupling constant of 16 Hz in the PMR spectrum), was confirmed by x-ray crystallographic analysis of a single crystal. A stereochemical model of the molecule of compound (III) is shown in Fig. 1. The atomic coordinates are given in Table 1. The bond lengths and bond angles, which do not differ from the normal values and do not require comment, are given in Tables 2 and 3. We mention only that the planes of the furan ring  $C_{(9)}C_{(10)}C_{(11)}C_{(12)}O_{(1)}$  and oxobutenyl fragment  $C_{(14)}C_{(15)}C_{(16)}O_{(2)}$  are turned to different sides of the plane of the indole fragment by 8.1 and 6.2° respectively. In the crystal of the ketone (III) the molecules are linked in pairs by two

\*For Communication 14, see [1].

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Fig. 1. Stereochemical models and the hydrogen bonds of the molecules of 3-(5-methyl-2-furyl)-2-(3oxo-1-butenyl)indole (III).

hydrogen bonds, formed by the hydrogen atom at the nitrogen atom in one of the molecules and the oxygen atom of the carbonyl group in the other. The hydrogen bond has the following parameters:  $O_{(2)} - H_{(1Na)}$  bond length 2.030(3) Å,  $O_{(2)} - H_{(1Na)} - N_{(a)}$  angle 151.1(2)°.

Initially [6] we assumed that the (Ia)  $\rightarrow$  (III) transformation took place through the intermediate formation of the hydroxylamine (IV) followed by attack by electrophilic nitrogen at position 2 of the furan ring.



To check this hypothesis we synthesized the hydroxylamine (IV) by the reduction of compound (Ia) with the  $Zn + NH_4Cl$  system or the complex thiolates of tin [8]. However, it was found that compound (IV) does not form the ketone (III) in the presence of acidic catalysts (perchloric acid, trimethylsilyl chloride, hydrochloric acid, boron trifluoride etherate, Amberlist 15). The direct formation of the product (III) was only observed with ferric chloride as catalyst.

On the other hand it was established that the hydroxylamine (IV), being an extremely unstable compound, forms a mixture of compounds during storage and purification by column chromatography. Thus, during an attempt at its purification on a column with  $Al_2O_3$  as adsorbent the azoxy derivative (Va) and the oxazine (VI) were isolated in addition to compound (IV) from the complex mixture of various products formed during elution and identified.



Atom	x	у	2	U(eq)
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O(1)	5237(3)	3742(1)	6275(2)	51(1)
O(2)	2108(4)	5423(1)	734(3)	71(1)
N	7542(4)	3977(1)	2094(3)	50(1)
C(1)	6483(5)	3979(1)	3270(4)	44(1)
C(2)	7355(5)	3592(1)	4461 (4)	43(1)
C(3)	9036(5)	3367(1)	3999(4)	44(1)
C(4)	10530(6)	2987(1)	4696(4)	53(1)
C(s)	11988(6)	2877(2)	3916(5)	<b>59</b> (1)
C(6)	11987(7)	3131(2)	2445(5)	61(1)
C(7)	10547(6)	3498(2)	1708(4)	55(1)
C(8)	9086(5)	3615(1)	2511(4)	45(1)
C(9)	6744(5)	3438(1)	5905(4)	46(1)
C(10)	7309(6)	3040(2)	7046(4)	61(1)
C(11)	6112(6)	3095(2)	8159(5)	67(1)
C(12)	4886(6)	3518(2)	7667(4)	55(1)
C(13)	3274(9)	3780(2)	8246(7)	76(1)
C(14)	4832(5)	4336(1)	3157(4)	47(1)
C(15)	4236(6)	4732(2)	2033(4)	53(1)
C(16)	2534(5)	5093(2)	1868(4)	51(1)
<b>C</b> (17)	1294(8)	5069(2)	3060(6)	63(1)

TABLE 1. Coordinates of the Nonhydrogen Atoms ( $\dot{A} \times 10^4$ ) and the Temperature Factors ( $\dot{A} \times 10^3$ ) of the Molecules of Compound (III)

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TABLE 2. Bond Lengths (d) in the Molecule of Compound (III)

Bond	d, Å	Bond	d, Å
O(1)-C(12)	1,375(4)	C(4)-C(5)	1,372(5)
O(1)-C(9)	1,381(4)	C(5)-C(6)	1,387(5)
O(2)-C(16)	1,225(4)	C(6)-C(7)	1,364(5)
NC(8)	1,360(4)	C(7)-C(8)	1,390(5)
NC(1)	1,383(4)	C(9)-C(10)	1,349(4)
C(1)-C(2)	I,395(4)	C(10)-C(11)	1,415(5)
C(1)-C(14)	1,422(4)	C(11)-C(12)	1,329(5)
C(2)-C(3)	1,433(4)	C(12)-C(13)	1,479(6)
C(2)-C(9)	1,442(4)	C(14)-C(15)	1,339(5)
C(3)-C(4)	1,401(5)	C(15)-C(16)	1,449(5)
C(3)-C(8)	1,402(4)	C(16)-C(17)	1,488(5)

The structure of compound (Va) was proved on the basis of data from the mass spectrum (m/z 547 M<sup>+</sup>) and PMR spectrum, in which a double set of signals for fragments A and B is observed. A feature of this spectrum is the strong downfield shift of the signal for the 3-H proton in the benzene ring of fragment A on account of the descreening effect of the N-O bond (8.06 ppm), whereas the multiplet signal of all the other aromatic protons is in the region of 7.43-7.25 ppm. The structure of compound (Va) was also confirmed by an alternative synthesis from the hydroxylamine (IV) in the presence of sodium methoxide.

On the basis of the PMR spectrum (see the Experimental section), mass spectrometry, and elemental analysis the second compound could be assigned structure (VI) or (VII). However, only an absorption band at 3380 cm<sup>-1</sup> was found in the IR spectrum of this compound. This may indicate the presence of the OH group, while the absence of absorption characteristic of the carbonyl group also favors the oxazinoindole structure (VI).

The product (VI) gradually accumulates during the storage of solutions of compound (IV) at room temperature. This process is accelerated if the hydroxylamine (IV) is boiled in toluene. These facts make it possible to suppose that the formation of the oxazine (VI) probably results from oxidation of the hydroxylamine (IV) by atmospheric oxygen. This is confirmed by the production of compound (VI) with an 80% yield during the oxidation of the hydroxylamine (IV) by potassium bichromate.

Angle	w, deg	Angle	ω, deg
C(12)-O(1)-C(9)	107,3(3)	NC(8)-C(3)	107,9(3)
$C_{(8)} - N - C_{(1)}$	110,4(3)	$C_{(7)}-C_{(8)}-C_{(3)}$	122,8(3)
N-C(1)-C(2)	107,7(3)	$C_{(10)} - C_{(9)} - O_{(1)}$	108,5(3)
N-C(1)-C(14)	121,7(3)	C(10)-C(9)-C(2)	134,0(3)
C(2)-C(1)-C(14)	130,6(3)	O(1)-C(9)-C(2)	117,5(3)
$C_{(1)}-C_{(2)}-C_{(3)}$	106,9(3)	C(9)-C(10)-C(11)	107,2(4)
$C_{(1)} - C_{(2)} - C_{(9)}$	128,1(3)	$C_{(12)} - C_{(11)} - C_{(10)}$	107,8(3)
C(3)-C(2)-C(9)	125,0(3)	$C_{(11)} - C_{(12)} - O_{(1)}$	109,3(3)
$C_{(4)} - C_{(3)} - C_{(8)}$	118,1(3)	$C_{(11)} - C_{(12)} - C_{(13)}$	135,1(4)
C(4)-C(3)-C(2)	134,8(3)	O(1)-C(12)-C(13)	115,6(4)
$C_{(8)} - C_{(3)} - C_{(2)}$	107,1(3)	$C_{(15)}-C_{(14)}-C_{(1)}$	125,5(3)
$C_{(5)} - C_{(4)} - C_{(3)}$	119,1(3)	$C_{(14)} - C_{(15)} - C_{(16)}$	126,6(3)
C(4)-C(5)-C(6)	121,1(4)	O(2)-C(16)-C(15)	119,7(3)
C(7)-C(6)-C(5)	121,9(4)	O(2)C(16)C(17)	119,3(3)
$C_{(6)} - C_{(7)} - C_{(8)}$	117,0(3)	C(15)-C(16)-C(17)	121,0(4)
N-C(8)-C(7)	129,3(3)	1	

TABLE 3. Bond Angles ( $\omega$ ) in the Molecule of Compound (III)

Our proposed mechanism for the formation of the oxazine (VI) includes an intramolecular Diels-Alder reaction between the furan ring and the nitroso group of the intermediate nitroso compound (VIII) followed by cleavage of the bridging ether bond in the strained adduct. Similar heterocycloaddition is well known and has already been considered [9] as the main stage in the synthesis of mitomycin.

The reduction of the oxazine (VI) in the  $SnCl_2 \cdot 2H_2O + HCl$  system leads quite smoothly to the formation of the indolenyl ketone (III). Thus, the most likely intermediate in the transformation of the methane derivative (Ia) during the production of the indole (III) can be considered to be the nitroso compound (VIII).



The direct transformation of the hydroxylamine (IV) into the ketone (III) in the presence of ferric chloride becomes understandable on the basis of the proposed mechanism. In this case the FeCl<sub>3</sub> promotes the oxidation of the initial compound (IV) to the oxazine (VI), and the FeCl<sub>2</sub> formed in the reaction acts as reducing agent for the latter. On the other hand, the fact that the reduction of (Ib) in the presence of  $SnCl_2 \cdot 2H_2O + HCl$  does not lead to an indole derivative but results in the formation of the amine (IIb) can also be explained, since in this case the nitroso group of the intermediate reduction product is deactivated under the influence of the donating solvent.

An attempt to obtain a hydroxylamine derivative from compound (Ib) by the above-mentioned methods was unsuccessful. Here the amine (IIb) was isolated as the main product, and the azoxy derivative (Vb) was a minor product.

In view of the certain analogy in the chemical characteristics of the phenol, hydroxyl, and acylamino groups in aromatic compounds, we obtained the acylamino derivatives (IXa, b) in order to convert them into tetracyclic derivatives of indole. In fact, the salts (Xa, b) were obtained during the reaction of these compounds with trityl perchlorate. In our opinion the mechanism of their formation hardly differs at all from the analogous mechanism in the case of the benzofuran derivatives [5].

In the PMR spectrum of the salt (Xb), recorded in deuterotrifluoroacetic acid at room temperature, there are double sets of signals for all the groups of equivalent protons (intensity ratios  $\sim 2:3$ ). In the corresponding spectrum of compound (Xa) the signals are broadened, indicating the presence of two conformers due to restricted rotation of the acetyl group.



## **EXPERIMENTAL**

The PMR spectra were recorded on Tesla BS-467 (60 MHz, internal standard HMDS) and Bruker AMX-400 (400 MHz, internal standard TMS) instruments. The mass spectra were obtained on a Varian MAT-112 mass spectrometer with direct injection into the ion source. The energy of the ionizing electrons was 70 eV. The temperature of the ionization chamber was 100-180°C. The reaction and the individuality of the final products were monitored by TLC on Silufol UV-254 plates; the eluant was chosen individually in each case.

**X-Ray Crystallographic Analysis of Compound (III).** The monoclinic crystals of (III) with composition  $C_{17}H_{15}NO_2$  were grown from methanol. Unit cell parameters: a = 6.9590(10), b = 24.230(6), c = 8.454(2) Å,  $\beta = 105.010(10)^\circ$ , V = 1376.8(5) Å<sup>3</sup>, space group P2(1)/c, Z = 4. The unit cell parameters and the intensities of 770 unique reflections with  $I > 2\sigma(I)$  were obtained on an Enraf-Nonius CAD-4 diffractometer without a monochromator (MoK<sub>a</sub> radiation,  $\theta/2\theta$  scan to  $2\theta = 45^\circ$ . The structure was interpreted by the direct method by means of the SHELXTL Plus software (PC version) and refined in anisotropic approximation (isotropic for the hydrogen atoms) to R = 0.0237 and  $R_w = 0.0607$ .

The atomic coordinates can be obtained from the authors.

Bis(5-methyl-2-furyl)-2-nitrophenylmethane (Ia) and bis(5-methyl-2-furyl)-4,5-dimethoxy-2-nitrophenylmethane (Ib) were obtained by the method described in [7].

**Bis(5-methyl-2-furyl)-2-aminophenylmethane (IIa).** To a stirred suspension of 10 g of zinc dust in 4 ml of trimethylchlorosilane and 50 ml of methanol we added 2.97 g (10 mmole) of compound (Ia) in 15 ml of dioxane. The mixture was stirred at room temperature until the initial compound had disappeared (monitored by TLC). It was then poured into water and extracted with ether. The extract was washed with sodium bicarbonate solution, dried with sodium sulfate, and evaporated to dryness. The product was then isolated on a small column of silica gel with methylene chloride – hexane as eluant. The yield was 1.87 g (70%).

B. To a solution of 1.0 g (3.4 mmole) of compound (Ia) in 15 ml of methanol we added successively 0.7 g of 5% Pd/C, 10 mg of FeCl<sub>3</sub>·H<sub>2</sub>O, and 0.33 ml of NH<sub>2</sub>NH<sub>2</sub>·H<sub>2</sub>O. The mixture was boiled for 4 h until the initial compound had disappeared. The cooled reaction mass was filtered, the filtrate was evaporated, the residue was chromatographed on a column of aluminum oxide with hexane, and the product (IIa) was isolated in the form of an oil. The yield was 0.6 g (65%). PMR spectrum (deuterochloroform,  $\delta$ , ppm): 7.12 (1H, ddd, J = 1.3, 8.0, 8.5 Hz, 4-H<sub>Ar</sub>); 6.90 (1H, dd, J = 1.3, 7.5 Hz, 6-H<sub>Ar</sub>); 6.77 (1H, ddd, J = 0.9, 7.5, 8.5 Hz, 5-H<sub>Ar</sub>); 6.71 (1H, dd, J = 0.9, 8.0 Hz, 3-H<sub>Ar</sub>); 5.93 (4H, s, H<sub>Fur</sub>); 5.41 (1H, s, CH); 3.67 (1H, bs, NH<sub>2</sub>); 2.28 (6H, s, CH<sub>3</sub>). Found %: C 76.38; H 6.41; N 5.24. Calculated %: C 76.41; H 6.38; N 5.27.

**Bis(5-methyl-2-furyl)-2-amino-4,5-dimethoxyphenylmethane (IIb).** The compound was obtained by method A with a yield of 73%; mp 81°C (hexane – methylene chloride). IR spectrum, cm<sup>-1</sup> (Vaseline oil, sodium chloride): 3450, 3380 (NH<sub>2</sub>). PMR spectrum, deuterochloroform ( $\delta$ , ppm): 6.41 (1H, s, 6-H<sub>Ar</sub>); 6.23 (1H, s, 3-H<sub>Ar</sub>); 5.83 (4H, s, H<sub>Fur</sub>); 5.27 (1H, s, CH); 3.73 (3H, s, OCH<sub>3</sub>); 3.62 (3H, s, OCH<sub>3</sub>); 3.20 (2H, bs, NH<sub>2</sub>); 2.18 (6H, s, CH<sub>3</sub>). Found %: C 69.71; H 6.47; N 4.28. C<sub>19</sub>H<sub>21</sub>NO<sub>4</sub>. Calculated %: C 69.75; H 6.51; N 4.26.

3-(5-Methyl-2-furyl)-2-(3-oxo-1-butenyl)indole (III). To a solution of 2.97 g (10 mmole) of compound (Ia) in 50 ml of ether we added a solution of 10 g of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 20 ml of hydrochloric acid and 20 ml of water. The mixture was stirred for 4-5 h at room temperature until the initial compound had disappeared. The ether layer was then separated, dried over calcined potassium carbonate, and evaporated. The residue was recrystallized from toluene. The yield was 1.4 g (53%); mp 216-217°C (toluene). IR spectrum, cm<sup>-1</sup> (Vaseline oil, sodium chloride): 3320 (NH), 1680 (CO). PMR spectrum, acetone-d<sub>6</sub> ( $\delta$ , ppm): 10.92 (1H, bs, NH); 8.12 (1H, d, J = 16 Hz,  $\beta$ -H); 7.91 (1H, dd, J = 8.0, 0.5 Hz, 4-H); 7.42 (1H, dd, J = 8.0, 0.5 Hz, 7-H); 7.29 (1H, m, J = 9.0, 8.0, 0.5 Hz, 5-H); 7.13 (1H, m, J = 9.0, 8.0, 0.5 Hz, 6-H); 6.78 (1H, d, J = 16 Hz,

 $\alpha$ -H); 6.68 (1H, d, J = 3.2 Hz, 3-H<sub>Fur</sub>); 6.25 (1H, d, J = 3.2 Hz, 4-H<sub>Fur</sub>); 2.43 (3H, s, CH<sub>3</sub>); 2.37 (3H, s, COCH<sub>3</sub>). Found %: C 76.96; H 5.70; N 5.28. C<sub>17</sub>H<sub>15</sub>NO<sub>2</sub>. Calculated %: C 76.91; H 5.67; N 5.32.

**Bis(5-methyl-2-furyl)-2-hydroxyaminophenylmethane (IV).** To a solution of 1.2 g (4 mmole) of compound (Ia) in 20 ml of THF we added 0.24 g of ammonium chloride in 8 ml of water and 1.12 g of zinc dust. The mixture was stirred at room temperature for 2 h until the initial compound had been completely consumed (TLC). It was then filtered, and the filtrate was diluted with water and extracted with ether. The extract was dried over sodium sulfate and evaporated at reduced pressure. The yield of the oily technical product, suitable for further syntheses, was 0.92 g (80%). PMR spectrum, deuterochloroform ( $\delta$ , ppm): 7.32-6.87 (4H, m, H<sub>Ar</sub>); 5.82 (4H, s, H<sub>Fur</sub>); 5.33 (1H, s, CH); 2.19 (6H, s, 2CH<sub>3</sub>).

During an attempt at the purification of compound (IV) by column chromatography on silica gel (eluant 1:1 petroleum ether-toluene) or aluminum oxide (eluant 5:1 petroleum ether-toluene) compounds (Va) and (VI) were isolated.

**2,2'-Di[bis(5-methyl-2-furyl)methyl]azoxybenzene (Va).** mp 131-132°C (hexane-benzene). PMR spectrum, deuterochloroform ( $\delta$ , ppm): 8.06 (1H, dd, J = 0.9, 8.0 Hz, 3-H<sub>Ar(A)</sub>); 7.43-7.25 (7H, m, 3-, 4-, and 5-H<sub>Ar(A)</sub> and 3-, 4-, 5-, and 6-H<sub>Ar(B)</sub>); 6.12 (1H, s, CH<sub>(A)</sub>); 5.99 (1H, s, CH<sub>(B)</sub>); 5.90 (2H, d, J = 3.2 Hz, 3-H<sub>Fur(A)</sub>); 5.87 (2H, d, J = 3.2 Hz, 3-H<sub>Fur(A)</sub>); 5.86 (2H, d, J = 3.2 Hz, 3-H<sub>Fur(B)</sub>); 5.83 (2H, d, J = 3.2 Hz, 4-H<sub>Fur(A)</sub>); 2.28 (3H, s, CH<sub>3</sub>); 2.17 (3H, s, CH<sub>3</sub>). Mass spectrum (m/z): 547 (M<sup>+</sup>). Found %: C 74.67; H 5.50; N 5.15. C<sub>34</sub>H<sub>30</sub>N<sub>2</sub>O<sub>5</sub>. Calculated %: C 74.70; H 5.53; N 5.13.

From compound (Ib) under the conditions for the synthesis of the product (IV) we obtained a mixture of products (IIb) and (Vb), which were separated by column chromatography on aluminum oxide with a 1:1 mixture of petroleum ether and diethyl ether as eluant. The yield of compound (IIb) was 65%, and the yield of compound (Vb) was 3%.

**2,2'-Di[bis(5-methyl-2-furyl)methyl]-4,4',5,5'-tetramethoxyazoxybenzene (Vb).** The yield was 3%; mp 151-152°C (hexane-benzene). PMR spectrum, deuterochloroform ( $\delta$ , ppm): 8.42 (1H, s, 3-H<sub>Ar(A)</sub>); 7.27 (1H, s, 3-H<sub>Ar(B)</sub>); 6.83 (1H, s, 6-H<sub>Ar(A)</sub>); 6.79 (1H, s, 6-H<sub>Ar(B)</sub>); 6.22 (1H, s, CH<sub>(A)</sub>); 6.16 (1H, s, CH<sub>(B)</sub>); 5.90 (2H, d, J = 3.2 Hz, 3-H<sub>Fur(A)</sub>); 5.86 (2H, d, J = 3.2 Hz, 4-H<sub>Fur(A)</sub>); 5.85 (2H, d, J = 3.2 Hz, 3-H<sub>Fur(B)</sub>); 5.82 (2H, d, J = 3.2 Hz, 4-H<sub>fur(A)</sub>); 3.93 (3H, s, OCH<sub>3</sub>); 3.86 (3H, s, OCH<sub>3</sub>); 3.83 (3H, s, OCH<sub>3</sub>); 3.82 (3H, OCH<sub>3</sub>); 2.20 (6H, s, 2CH<sub>3</sub>); 2.21 (6H, s, 2CH<sub>3</sub>). Mass spectrum (m/z): 667 (M<sup>+</sup>). Found %: C 68.49; H 5.75; N 4.15. C<sub>38</sub>H<sub>38</sub>N<sub>2</sub>O<sub>9</sub>. Calculated %: C 68.45; H 5.47; N 4.20.

2-Hydroxy-2-methyl-5-(5-methyl-2-furyl)-2H-1,2-oxazino[2,3-a]indole (VI). To a solution of 0.3 ml of sulfuric acid  $(d = 1.84 \text{ g/cm}^3)$  in 4 ml of water, cooled to 0°C, we added with vigorous stirring a solution of 0.92 g (3.2 mmole) of compound (IV) in 25 ml of THF and then a solution of 0.3 g (1 mmole) of potassium bichromate in 7 ml of water. The stirring was continued for 20 min, after which the reaction mixture was poured into water and extracted with ether. The extract was washed with a solution of sodium bicarbonate and with water, filtered through a layer of silica gel, and evaporated. We obtained 0.68 g (75%) of compound (VI) in the form of an oil. IR spectrum, cm<sup>-1</sup> (sodium chloride): 3380 (OH). PMR spectrum, deuterochloroform ( $\delta$ , ppm): 7.86 (1H, dd, J = 8.0, 0.5 Hz, 6-H); 7.50 (1H, dd, J = 8.0, 0.5 Hz, 9-H); 7.32-7.28 (1H, m, 7-H); 7.22 (1H, d, J = 10 Hz, 3-H); 7.20-7.16 (1H, m, 8-H); 6.50 (1H, d, J = 3.2 Hz, 3-H<sub>Fur</sub>); 6.12 (1H, d, J = 3.2 Hz, 4-H<sub>Fur</sub>); 6.06 (1H, d, J = 10 Hz, 4-H); 3.49 (1H, bs, OH); 2.42 (3H, s, CH<sub>3</sub>); 1.81 (3H, s, CH<sub>3</sub>). Mass spectrum (m/z): 281 (M<sup>+</sup>). Found %: C 72.58; H 5.37; N 4.98. C<sub>17</sub>H<sub>15</sub>NO<sub>3</sub>. Calculated %: C 72.62; H 5.38; N 5.01.

**Bis(5-methyl-2-furyl)-2-acetylaminophenylmethane (IXa).** A. To a solution of 2.67 g (10 mmole) of compound (IIa) in 10 ml of dioxane we added 1.18 ml (12.5 mmole) of acetic anhydride and 1.74 ml (12.5 mmole) of triethylamine. The mixture was stirred at room temperature for 5 min, and the product (VIIIa) was precipitated with an excess of water. After recrystallization from a mixture of hexane and methylene chloride we obtained 2.65 g of compound (IXa) (90%).

B. To a suspension of 20 g of zinc dust in 20 ml of acetic anhydride at room temperature we added with stirring a solution of 2.97 g (10 mmole) of compound (Ia) in 20 ml of dioxane. The reaction mixture was stirred for 1 h and filtered through a layer of silica gel, which was then washed with 20 ml of dioxane. The product (IXa) was precipitated from the filtrate with an excess of water and recrystallized from a mixture of hexane and methylene chloride. The yield was 2.24 g (80%); mp 136-137°C (hexane – methylene chloride). PMR spectrum, deuterochloroform ( $\delta$ , ppm): 7.79 (1H, d, J = 8.0 Hz, 6-H<sub>Ar</sub>); 7.58 (1H, bs, NH); 7.30-7.12 (3H, m, 3-, 4-, and 5-H<sub>Ar</sub>); 5.96-5.91 (4H, m, H<sub>Fur</sub>); 5.46 (1H, s, CH); 2.25 (6H, s, 2CH<sub>3</sub>); 2.01 (3H, s, COCH<sub>3</sub>). Found %: C 73.81; H 6.26; N 4.41. C<sub>19</sub>H<sub>19</sub>NO<sub>3</sub>. Calculated %: C 73.77; H 6.19; N 4.52.

**Bis(5-methyl-2-furyl)-2-acetylamino-4,5-dimethoxyphenylmethane (IXb).** The compound was obtained similarly to compound (IXa) by method B with a yield of 84%; mp 144-145°C (hexane – methylene chloride). PMR spectrum, deuterochloroform ( $\delta$ , ppm): 7.42 (1H, s, NH); 7.33 (1H, s, 6-H<sub>Ar</sub>); 6.63 (1H, s, 3-H<sub>Ar</sub>); 5.92-5.87 (4H, m, H<sub>Fur</sub>); 5.36 (1H, c, CH); 3.84 (3H, s, OCH<sub>3</sub>); 3.76 (3H, s, OCH<sub>3</sub>); 2.23 (6H, s, 2CH<sub>3</sub>); 2.00 (3H, s, COCH<sub>3</sub>). Found %: C 68.44; H 6.09; N 3.85. C<sub>21</sub>H<sub>23</sub>NO<sub>5</sub>. Calculated %: C 68.28; H 6.28; N 3.79.

2,4-Dimethylindolo[2,3-h]-1-oxazulenium Perchlorate (Xa). To a solution of 3.09 g (10 mmole) of the amide (VIIa) and 2.6 g (10 mmole) of triphenylmethanol in 10 ml of dioxane we added 0.4 ml of 70% perchloric acid, and we boiled the mixture for 5 min. After the reaction mixture had cooled, the precipitated product (Xa) was filtered off, washed with dioxane and with ether, and dried in air. The yield was 2.34 g (60%); decomp. p > 290°C. PMR spectrum, trifluoroacetic acid ( $\delta$ , ppm): 8.53 (1H, d, J = 11.2 Hz, 6-H); 8.52 (1H, d, J = 8.1 Hz, 11-H); 8.13 (1H, d, J = 11.2 Hz, 5-H); 7.69-7.65 (1H, m, 9-H); 7.57 (1H, d, J = 8.3 Hz, 8-H); 7.44-7.40 (1H, m, 10-H); 6.97 (1H, s, 3-H); 3.82 (3H, s, COCH<sub>3</sub>); 2.89 (3H, s, 2-CH<sub>3</sub>); 2.66 (3H, s, 4-CH<sub>3</sub>). Found %: C 58.50. H 4.17; Cl 9.05; N 3.60. C<sub>19</sub>H<sub>16</sub>ClNO<sub>6</sub>. Calculated %: C 58.54; H 4.14; Cl 9.10; N 3.59.

**2,4-Dimethyl-9,10-dimethoxyindolo[2,3-***h***]-1-oxazulenium Perchlorate (Xb).** This compound was obtained similarly to compound (Xa) with a yield of 65%. Two conformers were distinguished in the PMR spectrum. For the first conformer, PMR spectrum, deuterotrifluoroacetic acid ( $\delta$ , ppm): 9.44 (1H, d, J = 11.5 Hz, 6-H); 8.39 (1H, s, 11-H); 8.31 (1H, d, J = 11.5 Hz, 5-H); 7.73 (1H, s, 8-H); 7.19 (1H, s, 3-H); 4.06 (3H, s, OCH<sub>3</sub>); 4.02 (3H, s, OCH<sub>3</sub>); 3.02 (3H, s, COCH<sub>3</sub>); 2.99 (3H, s, 2-CH<sub>3</sub>); 2.79 (3H, s, 4-CH<sub>3</sub>). For the second conformer, PMR spectrum ( $\delta$ , ppm): 8.57 (1H, d, J = 11.5 Hz, 6-H); 8.16 (1H, s, 11-H); 8.12 (1H, d, J = 11.5 Hz, 5-H); 7.28 (1H, s, 8-H); 7.04 (1H, s, 3-H); 4.02 (3H, s, OCH<sub>3</sub>); 3.96 (3H, s, OCH<sub>3</sub>); 3.02 (3H, s, COCH<sub>3</sub>); 2.94 (3H, s, 2-CH<sub>3</sub>); 2.72 (3H, s, 4-CH<sub>3</sub>). The intensity ratio of the signals of the first and second conformers was ~3:2. Found %: C 56.02; H 4.52; Cl 7.93; N 3.13. C<sub>21</sub>H<sub>20</sub>ClNO<sub>8</sub>. Calculated %: C 56.07; H 4.48; Cl 7.88; N 3.11.

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