

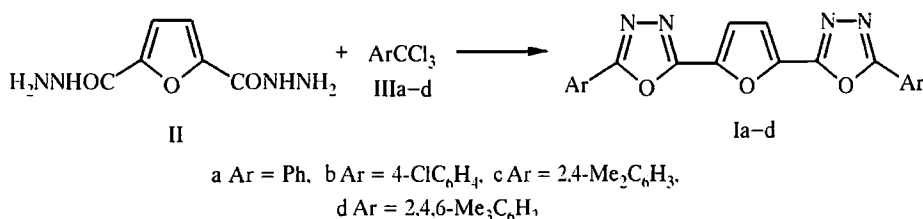
SYNTHESIS OF NOVEL 2,5-BIS(5-ARYL-1,3,4-OXADIAZOL-2-YL)FURANS FROM FURAN-2,5-DICARBOXYLIC ACID DIHYDRAZIDE AND TRICHLOROMETHYLARENES

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2,5-Bis(5-aryl-1,3,4-oxadiazol-2-yl)furans are synthesized via the reaction of trichloromethylarenes with furan-2,5-dicarboxylic acid dihydrazide. The structures of the products are confirmed by IR and mass spectra.

Among organic luminophores, which are widely used in scintillation techniques, one of the most effective is 1,4-bis(5-phenyl-1,3,4-oxadiazol-2-yl)benzene (PDPDP). Thus, many paths for preparing this compound and its derivatives have been developed [1-5]. The synthesis of heterocyclic analogs of PDPDP has been noted [6, 7] but only for 2,5-bis(5-aryl-1,3,4-oxadiazol-2-yl)thiophenes. Heterocyclic analogs of PDPDP containing a central furan ring have not been reported.

The present work involves the development of a convenient method for synthesizing 2,5-bis(5-aryl-1,3,4-oxadiazol-2-yl)furans Ia-d from furan-2,5-dicarboxylic acid dihydrazide (II) and trichloromethylarenes IIIa-d.



Compounds Ia-c were prepared by boiling the compounds II and III for 5 h in a methanol-pyridine mixture according to the literature method [8]; compound Id was obtained using *t*-butanol-2,6-lutidine mixture [9]. The properties of the 1,3,4-oxadiazoles Ia-d are listed in Table 1. The structure of these compounds agrees well with the results of elemental analysis and IR and mass spectra. Like for 1,4-phenylenebis-1,3,4-oxadiazoles [10], we could not use NMR spectroscopy to prove the structure of the novel 2,5-bis(5-aryl-1,3,4-oxadiazol-2-yl)-furans Ia-c owing to their low solubility. The PMR spectrum in DMF-*d*₇ could be recorded only for the methyl-substituted compound Id.

The IR spectra of Ia-d (Table 1) were interpreted according to the data compiled in a monograph [11] for 1,3,4-oxadiazoles and furans. In particular, the spectra contain strong absorption maxima in the 1630-1570 cm⁻¹ region, which are characteristic of stretching vibrations of the oxadiazole ring [11]. Absorption bands at 1040-1010 cm⁻¹ also arise from the stretching vibrations of the =C-O-C= fragment of these compounds [12].

Scheme 1 shows the principal fragmentation patterns of the synthesized compounds in electron-impact mass spectra. Compounds Ia-d are less stable toward electron impact than PDPDP and its derivatives [10], the mass spectra of which usually have the molecular ions as the base peaks. For Ia-d, the intensity of the molecular ions

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vary in the range 8-61% (Table 2). As a rule, the $[\text{ArCO}]^+$ ions exhibit the maximum intensity. The fragments $[\text{ArCN}]^+$ and $[\text{Ar}]^+$ also are characteristic of the electron-impact mass spectra of 2,5-bis(1,3,4-oxadiazol-2-yl)-furans. Noteworthy ions of medium intensity are $[\text{ArCNO}]^+$, $[\text{M} - \text{ArCNO}]^+$, $[\text{M} - \text{ArCNO} - \text{ArCN}_2]^+$, $[\text{M} - 2\text{ArCNO}]^+$, and $[\text{M} - 2\text{ArCO}]^+$. The structure of ion $[\text{M} - 2\text{ArCO}]^+$ with m/z 146 is at present difficult to conceptualize.

Scheme 1

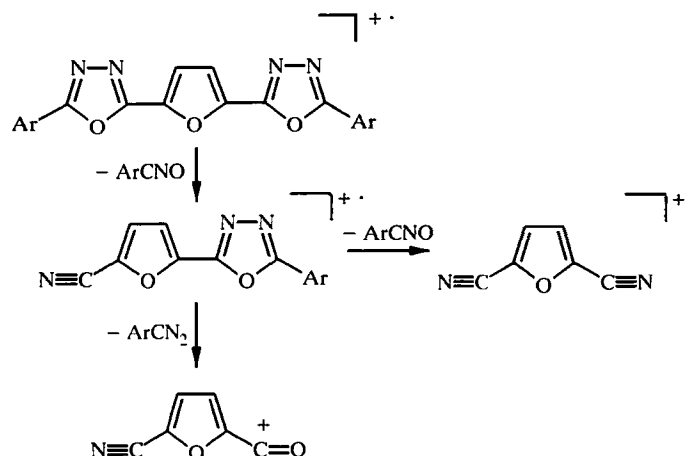


TABLE 1. Characteristics of 2,5-Bis(5-aryl-1,3,4-oxadiazol-2-yl)furans (Ia-d)

Com- pound	Empirical formula	Found, %			mp. °C (solvent)	IR spectrum, ν , cm^{-1}	Yield, %
		Calculated, %					
		C	H	N			
Ia	$\text{C}_{20}\text{H}_{12}\text{N}_4\text{O}_3$	$\frac{67.16}{67.41}$	$\frac{3.40}{3.39}$	$\frac{16.85}{15.72}$	276-277 (dioxane)	3112, 3088 ($\text{C}_{\text{Ar}}-\text{H}$) 1624, 1616, 1608, 1592, 1584, 1548 ($\text{C}=\text{N}$, $\text{C}=\text{C}$); 1032, 1024 ($\text{C}-\text{O}-\text{C}$); 856, 766, 728, 688 (δ $\text{C}_{\text{Ar}}-\text{H}$)	68
Ib	$\text{C}_{20}\text{H}_{10}\text{Cl}_2\text{N}_4\text{O}_3^*$	$\frac{56.27}{56.49}$	$\frac{2.38}{2.37}$	$\frac{13.10}{13.18}$	338-340 (DMF)	3144, 3088 ($\text{C}_{\text{Ar}}-\text{H}$); 1628, 1616, 1608, 1584, 1576 ($\text{C}=\text{N}$, $\text{C}=\text{C}$); 1028, 1016 ($\text{C}-\text{O}-\text{C}$); 856,838, 736, 696 (δ $\text{C}_{\text{Ar}}-\text{H}$)	47
Ic	$\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}_3$	$\frac{69.66}{68.89}$	$\frac{4.83}{4.89}$	$\frac{13.32}{13.59}$	216-218 (dioxane)	3128, 3040 ($\text{C}_{\text{Ar}}-\text{H}$); 2920 (CH_3); 1632, 1624, 1616, 1576 ($\text{C}=\text{N}$, $\text{C}=\text{C}$); 1032 ($\text{C}-\text{O}-\text{C}$); 824, 816, 808, 744, 696 (δ $\text{C}_{\text{Ar}}-\text{H}$)	56
Id	$\text{C}_{26}\text{H}_{24}\text{N}_4\text{O}_3^{*2}$	$\frac{70.89}{70.89}$	$\frac{5.41}{5.49}$	$\frac{12.86}{12.79}$	246-247 (dioxane)	3136, 3072 ($\text{C}_{\text{Ar}}-\text{H}$); 2960, 2944, 2920 (CH_3); 1620, 1592, 1560, 1540, 1528 ($\text{C}=\text{N}$, $\text{C}=\text{C}$); 1040, 1032, 1008 ($\text{C}-\text{O}-\text{C}$); 856, 800, 720, 712 (δ $\text{C}_{\text{Ar}}-\text{H}$)	75

* Found, %: Cl 16.41; calculated, %: Cl 16.68.

² PMR spectrum (ppm): 7.53 (2H, s, H_{fur}); 6.98 (4H, s, H_{arom}); 2.22 (6H, s, $p\text{-CH}_3$); 2.20 (12H, s, $o\text{-CH}_3$).

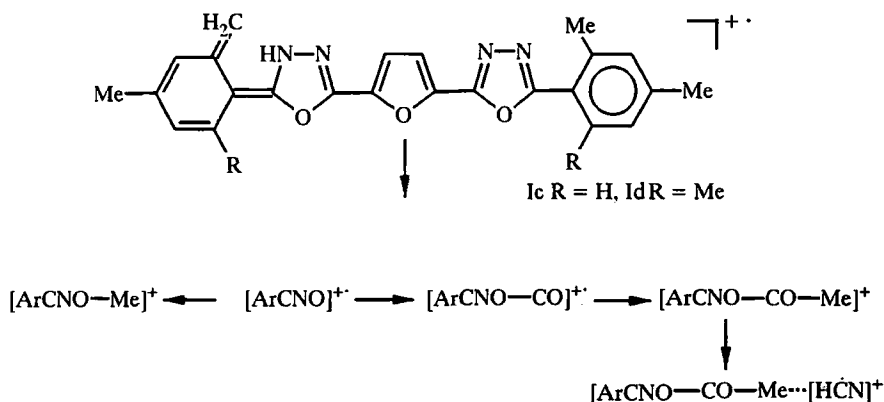
TABLE 2. Mass Spectral Characteristics of 2,5-Bis(5-aryl-1,3,4-oxadiazol-2-yl)furans (Ia-d)

Com- pound	Ion, m/z (I_{rel} , %)						Other ions
	$\frac{[M+1]^+}{[M]^+}$	$\frac{\Phi_1}{\Phi_2}$	$\frac{\Phi_3}{\Phi_4}$	$\frac{\Phi_5}{\Phi_6}$	$\frac{\Phi_7}{\Phi_8}$	$\frac{\Phi_9}{\Phi_{10}}$	
Ia	$\frac{357(10)}{356(33)}$	$\frac{300(2)}{244(6)}$	$\frac{237(4)}{146(3)}$	$\frac{119(5)}{127(10)}$	$\frac{105(100)}{103(87)}$	$\frac{120(13)}{77(90)}$	104(12) [PhCNH] ⁺ , 80(17), 76(59) [C ₆ H ₄] ⁺ , 75(15) [C ₆ H ₃] ⁺
Ib	$\frac{426(31)}{425(8)}$	$\frac{—}{313(14)}$	$\frac{—}{—}$	$\frac{153(6)}{151(1)}$	$\frac{139(100)}{137(44)}$	$\frac{—}{111(17)}$	113(5), 102(26), 80(9), 76(6) [C ₆ H ₄] ⁺ , 75(12) [C ₆ H ₃] ⁺
Ic	$\frac{413(8)}{412(43)}$	$\frac{356(8)}{—}$	$\frac{265(14)}{146(4)}$	$\frac{147(3)}{145(3)}$	$\frac{133(100)}{131(40)}$	$\frac{120(8)}{105(52)}$	182(7), 132(34) Φ_{11} , 119(6) Φ_{12} , 116(60) Φ_{13} , 104(26) Φ_{14} , 91(11) [C ₇ H ₇] ⁺ , 77(38) [C ₆ H ₅] ⁺
Id	$\frac{441(12)}{440(61)}$	$\frac{—}{—}$	$\frac{279(26)}{146(63)}$	$\frac{161(9)}{—}$	$\frac{147(45)}{145(74)}$	$\frac{120(11)}{119(15)}$	146(63) Φ_{11} *, 133(3) Φ_{12} , 130(100) Φ_{13} , 118(21) Φ_{14} *, 117(16) [Ar-2H] ⁺ , 106(3) [C ₈ H ₁₀] ⁺ , 91(11) [C ₇ H ₇] ⁺

Note. $\Phi_1 = [M-N_2-CO]^+$; $\Phi_2 = [M-2N_2-2CO]^+$; $\Phi_3 = [M-ArCNO]^+$; $\Phi_4 = [M-2ArCO]^+$; $\Phi_5 = [ArCNO]^+$; $\Phi_6 = [ArCN_2]^+$; $\Phi_7 = [ArCO]^+$; $\Phi_8 = [ArCN]^+$; $\Phi_9 = [M-ArCNO-ArCN_2]^+$; $\Phi_{10} = [Ar]^+$; $\Phi_{11} = [ArCNO-CH_3]^+$; $\Phi_{12} = [ArCNO-CO]^+$; $\Phi_{13} = [ArCN-CH_3]^+$; $\Phi_{14} = [ArCNO-CO-CH_3]^+$. Asterisks * denote Φ_{11} and Φ_{14} ions, which for compound Id have the same m/z values as Φ_4 and Φ_{10} ions, respectively.

Mass spectra of Ic,d, which have methyl groups in the *ortho* positions, contain fragments that do not appear in the spectra of Ia,b. These fragments probably result from a rearrangement of the molecular ion that includes transfer of hydrogen atom from the *o*-methyl group to the nitrogen atom of the oxadiazole ring [13]. This leads to the 1,3,4-oxadiazolinidene structure, which fragments further with cleavage of the N–N and C–O bonds, as shown in Scheme 2. The [ArCNO]⁺ ions arising from this apparently readily lose methyl radicals and CO

Scheme 2



molecules to produce $[\text{ArCNO} - \text{CH}_3]^+$, $[\text{ArCNO} - \text{CO}]^+$, and $[\text{ArCNO} - \text{CO} - \text{CH}_3]^+$ ions. The last ion is susceptible to the loss of HCN to give $[\text{ArCNO} - \text{CO} - \text{CH}_3 - \text{HCN}]^+$, which has the composition $[\text{C}_6\text{H}_5]^+$ and $[\text{C}_7\text{H}_7]^+$ for compounds **1c** and **1d**, respectively. The spectra of these compounds also have intense peaks corresponding to the loss of a methyl group from the $[\text{ArCN}]^+$ ion [9, 14].

EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer 577 spectrometer in KBr pellets. Mass spectra were obtained on a Kratos MS-30 mass spectrometer using direct-probe introduction into the ion chamber, 70 eV ionization potential, 0.1 mA emission current, and 250°C ionization chamber temperature. PMR spectrum of **1d** was recorded on a Bruker AM-300 (300 MHz) radiospectrometer in DMF-*d*₇. Melting points were measured on a Boetius stage and are uncorrected.

Commercially available dimethyl furan-2,5-dicarboxylate, benzotrichloride (**IIIa**), and 4-chlorobenzotrichloride (**IIIb**) were used. 2,4-Dimethylbenzotrichloride (**IIIc**) and 2,4,6-trimethylbenzotrichloride (**IIId**) were synthesized by electrophilic trichloromethylation of *m*-xylene [15] and mesitylene [16], respectively. Furan-2,5-dicarboxylic acid dihydrazide was prepared by boiling the corresponding dimethyl ester with a five-fold molar excess of hydrazine hydrate in methanol for 2 h. The dihydrazide **II** was obtained in 88% yield; mp 217–219°C (water); lit. mp 214–215°C [17].

2,5-Bis(5-aryl-1,3,4-oxadiazol-2-yl)furans (1a-c). Solution of hydrazide **II** (0.5 g, 2.7 mmol) and trichloromethylarene **IIIa-c** (5.4 mmol) in methanol (10 ml) and pyridine (5 ml) was boiled for 5 h. The precipitate that formed upon cooling was filtered off, washed with methanol, and recrystallized from the solvent indicated in Table 1.

2,5-Bis[5-(2,4,6-trimethylphenyl)-1,3,4-oxadiazol-2-yl]furan (1d) was prepared analogously to compounds **1a-c** using *t*-butanol–2,6-lutidine mixture (2:1 by volume) as solvent.

The properties of the synthesized compounds are listed in Tables 1 and 2.

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