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

S. I. Luiksaar, L. I. Belen'kii, and M. M. Krayushkin

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(3-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 trichloromethylarenones IIIa-d.

\[ \text{H}_2\text{NNHOC} + \text{ArCCl}_3 \rightarrow \text{ArCONNH}_2 \]

Ia-d

\[ \text{a Ar = Ph, b Ar = 4-ClC}_6\text{H}_4, \text{ c Ar = 2,4-Me}_2\text{C}_6\text{H}_3, \text{ d Ar = 2,4,6-Me}_3\text{C}_6\text{H}_2 \]

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-d6 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
vary in the range 8-61% (Table 2). As a rule, the [ArCO]$^+$ ions exhibit the maximum intensity. The fragments [ArCN]$^+$ and [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 [ArCNO]$^+$, [M - ArCNO]$^+$, [M - ArCNO - ArCN$^2$]$^+$, [M - 2ArCNO]$^+$, and [M - 2ArCO]$^+$. The structure of ion [M - 2ArCO]$^+$ with $m/z$ 146 is at present difficult to conceptualize.

Scheme 1

\[
\begin{align*}
\text{ArCN} & \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{N} & \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{ArCNO} & \quad \text{ArCNO} \\
\text{ArCN} & \quad \text{ArCNO} \\
\text{ArCN} & \quad \text{ArCNO} \\
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Empirical formula</th>
<th>Found, %</th>
<th>Calculated, %</th>
<th>mp, °C (solvent)</th>
<th>IR spectrum, $v$, cm$^{-1}$</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>C$<em>{20}$H$</em>{12}$N$_4$O$_3$</td>
<td>67.16</td>
<td>67.41</td>
<td>16.85, 15.72</td>
<td>276-277 (dioxane)</td>
<td>68</td>
</tr>
<tr>
<td>Ib</td>
<td>C$<em>{20}$H$</em>{12}$Cl$_2$N$_4$O$_3$*</td>
<td>56.27</td>
<td>56.49</td>
<td>13.10, 13.18</td>
<td>338-340 (DMF)</td>
<td>47</td>
</tr>
<tr>
<td>lc</td>
<td>C$<em>{24}$H$</em>{20}$N$_4$O$_3$</td>
<td>69.66</td>
<td>68.89</td>
<td>13.32, 13.59</td>
<td>216-218 (dioxane)</td>
<td>56</td>
</tr>
<tr>
<td>ld</td>
<td>C$<em>{26}$H$</em>{24}$N$_4$O$_3$*</td>
<td>70.89</td>
<td>70.89</td>
<td>12.86, 12.70</td>
<td>246-247 (dioxane)</td>
<td>75</td>
</tr>
</tbody>
</table>

* Found, %: Cl 16.41; calculated, %: Cl 16.68.
* PMR spectrum (ppm): 7.53 (2H, s, $H_{ar}$); 6.98 (4H, s, $H_{arom}$); 2.22 (6H, s, $p$-CH$_3$); 2.20 (12H, s, $o$-CH$_3$).