2,2-DIMETHYL-5-(5-R-2-FURFURYLIDENE)-1,3-DIOXANE-4,6-DIONES.

4. *SYNTHESIS, STEREOSTRUCTURES, AND PROPERTIES OF THIOPHENE ANALOGS*

G. D. Krapivin, V. G. Kul’nevich, and N. I. Val'ter

The reaction of 2-formylthiophenes with Meldrum’s acid gave the corresponding thenylidenedioxanediones, which, in contrast to the furfurylidene derivatives, have an s-trans conformation of the mutual orientation of the thiophene ring and the exocyclic double bond. Thenylidioxanediones were synthesized by the selective hydrogenation of the exocyclic double bond.

It has been shown [2] that furan aldehydes react with 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum’s acid) under mild conditions. These conditions were also used for the synthesis of thenylidene derivatives IIa-d, which were isolated in rather high yields in the form of colored crystals when the reaction mixtures were cooled (Table I).

"Hard" nucleophiles ("OH, "OR) add reversibly to the α-carbon atom of the exocyclic double bond. However, attempts to determine the pKₐ values of II were unsuccessful; in aqueous solutions with pH > 7, II decomposes rapidly to the anion of Meldrum’s acid and the corresponding 2-formylthiophene I.

"Soft" nucleophiles smoothly replace halogen atoms in the 5 (but not the 4!) position of the thiophene ring of IIc, d. In particular, the corresponding amino derivatives IIe, f were obtained by the reaction of bromo derivative IIc with a twofold excess of dimethylamine or morpholine.

The electronic absorption spectra (Table I) of the thenylidenedioxanediones are similar to the spectra of the corresponding furan derivatives. The differences between the wavelengths of the maxima of IIa-f and their furan analogs are 0, -10, -3, 2, 15, and 3 nm, respectively.

*See [1] for Communication 3.

### TABLE 1. Characteristics of II and III

<table>
<thead>
<tr>
<th>Compound</th>
<th>Empirical formula</th>
<th>mp, °C</th>
<th>UV spectrum (ethanol), λ&lt;sub&gt;max&lt;/sub&gt;, nm (log ε)</th>
<th>IR spectrum (ethanol), ν&lt;sub&gt;CO&lt;/sub&gt;, cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Yield, %</th>
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<tr>
<td>II&lt;sub&gt;a&lt;/sub&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;NO&lt;sub&gt;3&lt;/sub&gt;S</td>
<td>190...191</td>
<td>264 (3.76), 313 (3.80), 1702</td>
<td>1750</td>
<td>93</td>
</tr>
<tr>
<td>II&lt;sub&gt;b&lt;/sub&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;NO&lt;sub&gt;3&lt;/sub&gt;S</td>
<td>190...191</td>
<td>264 (3.76), 313 (3.80), 1702</td>
<td>1750</td>
<td>93</td>
</tr>
<tr>
<td>II&lt;sub&gt;c&lt;/sub&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;NO&lt;sub&gt;3&lt;/sub&gt;S</td>
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<td>1750</td>
<td>93</td>
</tr>
<tr>
<td>II&lt;sub&gt;d&lt;/sub&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;NO&lt;sub&gt;3&lt;/sub&gt;S</td>
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<td>93</td>
</tr>
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</table>

Compounds II<sub>a</sub>-d have broad (Δν<sub>1/2</sub> ~ 4000 cm<sup>-1</sup>), smooth, and symmetrical long-wave absorption bands that undergo a bathochromic shift with an increase in the polarity of the solvent (positive solvatochromism).

Amino derivatives II<sub>e</sub>,<sub>f</sub>, like merocyanine dyes, have, in the visible region of the spectrum, a narrow (Δν<sub>1/2</sub> 1600 cm<sup>-1</sup>) more intense band, on the shortwave slope of which one observes a second maximum (in the form of a shoulder) that is associated with a vibrational 0--1<sup>'</sup> transition. The latter, like the 0--0<sup>'</sup> transition, is polarized along the conjugation chain. (The absorption bands of 5-aminofurfurylidenedioxanediones also have a similar form [2].) The longwave absorption of II<sub>e</sub>,<sub>f</sub> has negative solvatochromism; this is characteristic for compounds, the ground state of which is more polar than the excited state.

The IR spectra of thenylidene compounds II contain two bands of stretching vibrations of C=O groups - asymmetrical and symmetrical; the ν<sub>CO</sub><sup>as</sup> band is approximately twice as intense as the ν<sub>CO</sub><sup>as</sup> band (Table 1).

In previous communications [2, 5, 6] it has been demonstrated by PMR spectroscopy and X-ray diffraction analysis that furfurylidenedioxanediones have an s-cis conformation that is stabilized by conjugation and an intramolecular hydrogen bond between the furan 3-H proton and the oxygen atom of the more closely located carbonyl group. In the PMR spectra this shows up in the form of a paramagnetic anisotropic shift of the signal of the 3-H proton to the 8.3-8.9 ppm region; the constant of spin-spin coupling between the 4-H and α-H protons is 0.6-0.8 Hz [2, 5].

In the PMR spectra of thenylidene derivatives II (Table 2) the signal of the 3-H proton does not undergo an anisotropic shift and is located at 7.75-7.90 ppm; spin-spin coupling (SSC) between the 4-H and α-H protons also is not observed. On the other hand, the spectrum of unsubstituted thenylidene derivative II<sub>a</sub> contains long-range SSC between the 5-H and α-H protons (J = 1.2 Hz), which constitutes evidence for a W-shaped orientation of the bonds between these rings, i.e., an s-transoid orientation of the thiophene ring and the exocyclic double bond. The low-temperature PMR spectra (−80°C) do not reveal broadening of the signals of the protons of the thiophene ring, and, consequently, in solution there is only one rotational conformer. The absence of a paramagnetic anisotropic effect of the carbonyl group on the 3-H proton and the existence of a long-range stereospecific SSC between the α-H and 5-H protons make it possible to conclude that II exist in the form of s-trans conformers. This difference in the conformational structures between the thenylidene and furfurylidene derivatives may be due to the possibility of specific intramolecular interaction between the sulfur atom and the oxygen atom of the carbonyl group, which is apparently energetically more favorable than the formation of an intramolecular hydrogen bond in 2,2-dimethyl-5-(5-R-furfurylidene)-1,3-dioxane-4,6-diones.

We have previously shown [2, 5] that the transfer of electron density in aminofurfurylidenedioxanedione molecules leads to an increase in the difference between the chemical shifts of the B protons of the furan ring and the constants of SSC between these rings.

Only an increase in the difference in the chemical shifts of the B protons of the thiophene ring (from 0.6 ppm for II<sub>a</sub>-d to 1.3 ppm for II<sub>e</sub>,<sub>f</sub>; Table 2) is observed in the PMR spectra of aminothiophenes II<sub>e</sub>,<sub>f</sub>.