Methyl 4,5-dibromofuran-2-carboxylate. This ester was obtained by bromination of methyl furan-2-carboxylate in excess of AlCl₃ without a solvent by the method in [2].

Samples of methyl 5-chloro-[2], 5-bromo-[11], 4-bromo-, and 5-chloro-4-bromofuran-2-carboxylate [2] were obtained from the corresponding aldehydes by oxidation with silver oxide and subsequent esterification with methanol in the presence of sulfuric acid.

LITERATURE CITED

5-ARYLFURAN-2,3-DIONES*

5-Arylfuran-2,3-diones were obtained by cyclization of aroylpyruvic acids in the presence of thionyl chloride. It is shown that the five-membered ring of 5-arylfuran-2,3-diones is unstable and is cleaved under mild conditions under the influence of nucleophilic reagents.

In contrast to their isomers, extremely little study has been devoted to arylfuran-2,3-diones. Only one study devoted to the synthesis of 4-benzoyl-5-phenylfuran-2,3-dione from oxalyl chloride and dibenzoylethylene is known [1].

We have found that cyclization, the products of which are 5-arylfuran-2,3-diones (II), occurs in the reaction of aroylpyruvic acids (I with thionyl chloride (see Table 1).

A band corresponding to the vibrations of the ethylene bond appears in the IR spectra of the cyclization products. The characteristic band of the carbonyl group is shifted from 1625 (in the spectra of the starting compounds) to 1713 cm⁻¹. The absorption band of the lactone grouping, in conformity with the literature data [2], is found at 1840 cm⁻¹.

\[
\text{SOCl}_2 + \text{RCOCH}_2\text{COOH} \rightarrow \text{RCOCH}_2\text{COOCOR} \quad \text{SOCl}_2
\]

I, II \( R = H, \text{CH}_3, \text{CH}_3\text{O, Br, Cl} \)

*Communication I from the series "Chemistry of Oxalyl Derivatives of Methyl Ketones."


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TABLE 1. 5-Arylfuran-2,3-diones (II)

<table>
<thead>
<tr>
<th>R</th>
<th>mp, °C</th>
<th>Empirical formula</th>
<th>Found, %</th>
<th>Calculated, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>H</td>
<td>133-134</td>
<td>C_{10}H_{14}O_3</td>
<td>68.6</td>
<td>4.5</td>
</tr>
<tr>
<td>CH₃</td>
<td>131-132</td>
<td>C_{11}H_{16}O_3</td>
<td>71.9</td>
<td>4.4</td>
</tr>
<tr>
<td>CH₂O</td>
<td>134-135</td>
<td>C_{11}H_{16}O_3</td>
<td>64.8</td>
<td>4.0</td>
</tr>
<tr>
<td>Cl</td>
<td>105-106</td>
<td>C_{12}H_{16}ClO_2</td>
<td>57.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Br</td>
<td>138</td>
<td>C_{12}H_{16}BrO_3</td>
<td>46.7</td>
<td>1.7</td>
</tr>
</tbody>
</table>

A singlet at 4.1 ppm corresponding to the \( =CH \)-proton and a group of signals centered at 9.15 ppm corresponding to the protons of the phenyl ring are present in the PMR spectrum.

The cyclization of I leads to a bathochromic shift of the long-wave maximum in isooctane from 310 to 340 nm (Fig. 1). However, the UV spectrum of II in alcohol is identical to the spectrum of I, and this constitutes evidence for ring opening under these conditions.

The formation of the corresponding furan-2,3-dione was not observed in the case of mesitoylpyruvic acid, evidently because of the steric hindrance created by the o-methyl groups.

When II is heated above its melting point it undergoes decomposition with carbon monoxide evolution, and it also reacts with o-phenylenediamine to give 2-phenacyl-3-quinoxaline (III).

\[
\text{H} \quad \text{N} \quad \text{CH}_2\text{COC}_6\text{H}_5
\]

The reaction of II with aniline proceeds with opening of the furan ring to give aroylpyruvic acid amides (IV).

The reaction of II with phenyl isocyanate gives 3,6-diphenyl-3,4-dihydro-1,3-oxazine-2,4-dione (V).

**EXPERIMENTAL**

The UV spectra of ethanol and dry hexane solutions of the compounds \((10^{-4} \text{ M})\) were recorded with an SF-4 spectrophotometer. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. The PMR spectra of 10% solutions of the compounds in CDCl₃ were recorded with a JNM-C-60HL spectrometer with hexamethyldisiloxane as the standard.

5-Arylfuran-2,3-diones (II). A 0.176-mole sample of thionyl chloride was added with stirring to 0.088 mole of benzoylpyruvic acid dissolved in 30 ml of dry benzene, after which the mixture was heated for 5 h on a water bath while maintaining the temperature within the flask at 65-70°. The mixture was then cooled, and the resulting yellow crystalline precipitate was removed by filtration and recrystallized from toluene.