Methyl 4,5-Dibromofuran-2-carboxylate. This ester was obtained by bromination of methyl furan-2-carboxylate in excess of $AlCl_3$ 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 esterfication with methanol in the presence of sulfuric acid.

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5-ARYLFURAN-2,3-DIONES*

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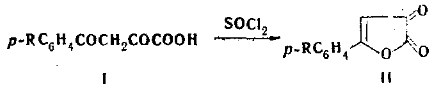
5-Arylfuran-2,3-diones were obtained by cyclization of aroylpyruvic acids in the presence of thionyl chloride. It is shown that the five-membered ring of 5-arylfuran-2,3-diones is unstable and is cleaved under mild conditions under the influence of nucleophilic reagents.

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 dibenzoylmethane 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}.



I II

I, II R = H, CH_3, CH_3O, Br, Cl

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

R	mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
			C	H	Hal	C	H	Hal	
H	133—134	$C_{10}H_6O_3$	68,6	3,7		68,9	3,4		59
CH_3	131—132	$C_{11}H_8O_3$	71,0	4,4		71,3	4,2		95
CH_3O	134—135	$C_{11}H_8O_4$	64,8	4,0		64,7	3,9		72
Cl	105—106	$C_{10}H_5ClO_3$	57,3	2,2	16,7	57,5	2,3	17,0	84
Br	136	$C_{10}H_5BrO_3$	46,7	1,7	31,4	47,0	1,9	31,6	49

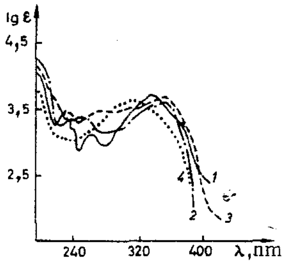


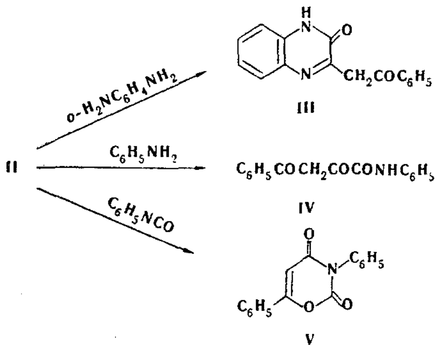
Fig. 1. UV spectra in isooctane of 5-arylfuran-2,3-diones: 1) 5-phenylfuran-2,3-dione; 2) 5-(p-tolyl)furan-2,3-dione; 3) 5-(p-bromophenyl)-furan-2,3-dione; 4) 5-phenylfuran-2,3-dione (in alcohol).

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-quinoxalone (III).



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} 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 $CDCl_3$ were recorded with a JNM-C-60HL spectrometer with hexamethylidisiloxane 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.

2-Phenacyl-3-quinoxalone (III). A solution of 0.01 mole of o-phenylenediamine in 50 ml of dry benzene was added to 0.01 mole of 5-phenylfuran-2,3-dione in 200 ml of dry benzene, after which the mixture was allowed to stand for several hours. The resulting precipitate was removed by filtration to give 1.9 g (75%) of a yellow crystalline substance with mp 267-268° (from ethanol). Found: N 10.50%. $C_{16}H_{12}N_2O_2$. Calculated: N 10.60%.

No melting-point depression was observed for a mixture of the above product with 2-phenacyl-3-quinoxalone obtained from o-phenylenediamine and methyl benzoylpyruvate.

Benzoylpyruvic Acid Phenylamide (IV). A solution of 0.011 mole of aniline in 15 ml of dry benzene was added to a solution of 0.011 mole of 5-phenylfuran-2,3-dione in 150 ml of dry benzene, after which the solvent was removed to give 2.9 g (94.7%) of a product with mp 118° (from toluene). Found: N 5.41%. $C_{16}H_{13}NO_3$. Calculated: N 5.24%. No melting-point depression was observed for a mixture of the above product with benzoylpyruvic acid phenylamide obtained from methyl phenyloxamate and acetophenone in the presence of sodium methoxide.

3,6-Diphenyl-3,4-dihydro-1,3-oxazine-2,4-dione (V). A 0.044-mole sample of phenyl isocyanate was added to a solution of 0.011 mole of 5-phenylfuran-2,3-dione in 150 ml of dry benzene, after which the mixture was heated at 80° for 2 h. The resulting precipitate was removed by filtration to give 2.18 g (72%) of a product with mp 237-238° (from ethanol). Found: N 5.41%. $C_{16}H_{11}NO_3$. Calculated: N 5.27%.

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RESEARCH ON VINYL ESTERS OF THE FURAN SERIES

XII*. REACTION OF VINYL ESTERS OF FURANCARBOXYLIC ACIDS WITH AMINES AND AZOLES

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The reaction of vinyl esters of furan-2-carboxylic, 5-bromofuran-2-carboxylic, and trans-β-(2-furyl)acrylic acids with aliphatic, aromatic, and heterocyclic amines was investigated. It was established that azoles add to the double bond of the vinyloxy group of the ester in conformity with the Markownikoff rule. α-(1-Azolyl)ethyl esters of the furan-2-carboxylic and β-(2-furyl)acrylic acids were synthesized. Acylation of the amines takes place during the reaction of vinyl esters of the furan series with diethylamine, aniline, p-vinyloxyaniline, morpholine, and piperidine.

The synthesis of esters containing an azole ring or another cyclic amine fragment in addition to a furan ring seems of interest for the preparation of substances with biological activity and complexing properties. The reactions of vinyl esters of acids of the furan series with amines have not been studied.

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*See [1] for communication XI.

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