IR spectra of the compounds were obtained with Specord and UR-20 spectrometers. The UV spectra of aqueous ethanol solutions of the compounds were recorded with a Specord spectrophotometer.

The 2-furyl-1,3-dioxanes (Ia-d) were synthesized by the method in [11]. The Raney nickel catalyst was prepared by the method in [12].

<u>Hydrogenation</u>. A catalytic hydrogenating flask was charged with 1-2 g of the catalyst, 0.01 mole of the starting dioxane, and 40 ml of ethanol, and the reaction was carried out at 60° in a stream of hydrogen with vigorous stirring for 5-8 h. Electrolytic hydrogen was used without additional purification.

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RING OPENING IN 5-ARYL-2,3-FURANDIONES

SYNTHESIS OF AROYLPYRUVIC ACID ESTERS*

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Aroylpyruvic acid esters are formed by the action of alcohols and phenol on 5-aryl-2,3-furandiones.

5-Aryl-2,3-furandiones (I) are unusually easily decyclized under the influence of nucleophilic reagents [2]. The rings of I are also opened by alcohols to give aroylpyruvic acid esters (II) (Table 1).

R = 0 + R'OH --- RCOCH₂COCOOR'

Of the aroylpyruvic acid esters, only the methyl and ethyl esters, obtained by Claisen reaction [3] in methanol or ethanol, have been accessible, regardless of the character of the alkyl group in the oxalic acid

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TABLE 1. Aroylpyruvic Acid Esters II

Com- pounds II	mp. °C	Reac. time,	Temp. °C	Found, %			Emp iric al	Calc., %			UV spec.		d, %
	. 17	min		с	н	Βτ	formula	с	11	Br	λ _{max} . nm	lgε	Yiel
a b c d e f g f i	58-598082881021043940382782834345	58 70 77 42 15 25 25 90 180	20 20 20 80 80 80 100 100	63,9 65,9 65,6 46,2 66,0 67,0 68,0 62,9 73,3	5.2 5.4 4,8 2,9 5.1 6,1 6,7 4,5 4,8	 27,7 	$\begin{array}{c} C_{11}H_{10}O_4\\ C_{12}H_{12}O_4\\ C_{12}H_{12}O_5\\ C_{11}H_9O_4Br\\ C_{12}H_{12}O_4\\ C_{13}H_{14}O_4\\ C_{13}H_{16}O_4\\ C_{13}H_{16}O_4\\ C_{15}H_{12}O_4\\ \end{array}$	64.6 66.2 65.0 46.3 66.2 66.6 67.7 63.4 72.8	$\begin{array}{r} 4.9 \\ 5.5 \\ 5.0 \\ 3.1 \\ 5.5 \\ 5.9 \\ 6.4 \\ 4.0 \\ 4.5 \end{array}$	 28.0 	311 313 330 325 311 336 312 312 312 332	3,50 3,15 3,43 3,21 3,17 3,91 3,18 3,17 3,72	87 86 52 43 68 69 74 96 82

ester [4]. Esterification of the unstable free acids is ineffective. Considering this, the discovered transformation can be regarded as a preparative method for the synthesis of esters II. Primary alcohols open the ring of I at 20°C in 1.5 h, whereas secondary alcohols open the rings of I at 80-100°C in 30 min, and phenol opens the rings in 3 h. Tertiary alcohols also decyclize furans I in 3 h at 60°, but the unsaturated hydrocarbon and the aroylpyruvic acid were isolated in this case.

The introduction of aroyl groups in the 4 position of 5-aryl-2,3-furandiones leads to an increase in the instability of the compounds, and III is cleaved instantly by methanol at room temperature:

$$c_6H_5CO + CH_3OH \rightarrow C_6H_5COCH_2COC_6H_5 + (COOCH_3)_2$$

EXPERIMENTAL

The UV spectra of 10^{-4} M solutions of the compounds in alcohol were recorded with a Specord UV-Vis spectrophotometer.

Aroylpyruvic Acid Esters (Πa -i). A 50-fold excess of alcohol was added to 1 g of I, and the mixture was maintained at the appropriate temperature until the solution became colorless. The excess alcohol was evaporated, and the product was recrystallized from toluene. The synthesized Πa -i are presented in Table 1. No melting-point depressions were observed for mixtures of esters Πa -e with authentic samples [5].

Phenyl Benzoylpyruvate (IIi). A 0.26-g (2.8 mmole) sample of phenol was added to 0.5 g (2.8 mmole) of I, and the mixture was heated in toluene at 100° for 3 h. The toluene was then evaporated to give 1.3 g (82%) of IIi.

Reaction of III with Methanol. A 50-fold excess of methanol was added to 1 g of III. Evaporation of the methanol at reduced pressure gave 0.6 g (75%) of dibenzoylmethane with mp 76°C (from petroleum ether). Found: C 80.5; H 5.5%. $C_{15}H_{12}O_2$. Calculated: C 80.1; H 5.4%. No melting-point depression was observed for a mixture of a sample of this product with an authentic sample.

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