REACTION OF 6-ARYL-2,2-DIMETHYL-1,3-DIOXIN-4-ONES WITH ACETYLACETONE AND METHYL ACYLPYRUVATES

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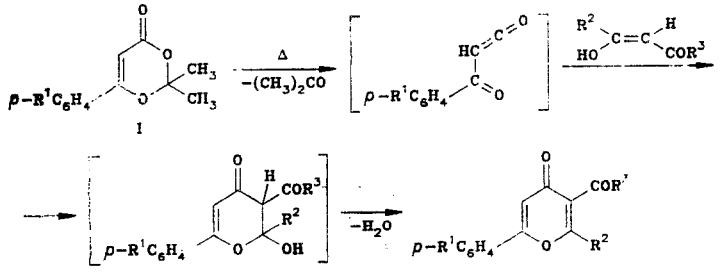
Aroyl ketenes formed in the thermolysis of 6-aryl-2,2-dimethyl-1,3-dioxin-4-ones undergo a [4π + 2π]-cycloaddition reaction with acetylacetone and methyl acylpyruvates to give 2-methyl- and 2-methoxycarbonyl-3-acyl-6-arylpyran-4-ones, respectively.

It has been previously shown that aroyl ketenes generated in the thermolysis of 5-aryl-2,3-dihydrofuran-2,3-diones undergo [4π + 2π]-cycloaddition reactions with aldehydes and ketones to give 6-aryl-1,3-dioxin-4-ones [1]. β-Dicarbonyl compounds that are incapable of undergoing enolization also react similarly [2]. In the reaction with phenols aroyl ketenes enter into aroylacetylation of the latter, the products of which are phenyl esters of aroylacetic acids [3].

Neither products of a [4π + 2π]-cycloaddition reaction nor products of aroylacetylation at the enol hydroxy group were isolated in an investigation of the reaction of aroyl ketenes generated in the thermolysis of 5-aryl-2,3-dihydrofuran-2,3-diones with completely enolized β-dicarbonyl compounds. Dimers of aroyl ketenes – 6-aryl-3-aroyl-4-hydroxypyran-2-ones – were isolated as the only reaction products in the case of diaroylmethanes and esters and amides of acylpyruvic acids [1]. 6-Aryl-2-methyl-2-phenyl-1,3-dioxin-4-ones, the formation of which is possible in the case of cleavage under conditions of reaction of the starting acids to the corresponding acetophenones, were obtained in the case of aroylpyruvic acids [4]. In this connection it seemed of interest to subject aroyl ketenes generated in the thermolysis of 6-aryl-2,2-dimethyl-1,3-dioxin-4-ones at a higher temperature (and, as a consequence of this, more reactive) with completely enolized β-dicarbonyl compounds.

It was established that 6-aryl-2,2-dimethyl-1,3-dioxin-4-ones I react with acetylacetone and methyl acetyl- and aroyl-pyruvates in dry refluxing xylene or on fusion at 140-145°C with the formation of, respectively, 2-methyl- and 2-methoxycarbonyl-6 aryl-3-acylpyran-4-ones II–XI.



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II–XI

II, III $R^2=R^3=CH_3$, II $R^1=CH_3$, III $R^1=Cl$; IV–VI $R^2=COOCH_3$, $R^3=CH_3$, IV $R^1=H$, V $R^1=Cl$, VI $R^1=Br$; VII–X $R^2=COOCH_3$, $R^3=C_6H_5$, VII $R^1=H$, VIII $R^1=CH_3$, IX $R^1=Cl$, X $R^1=Br$; XI $R^1=H$, $R^2=COOCH_3$, $R^3=p$-ClC_6H_4

The formation of pyranones II–XI is a consequence of [4π + 2π] cycloaddition of the intermediately formed aroyl ketenes at the double bond of the enol; the 2-substituted 6-aryl-3-acyl-2,3-dihydro-4-pyranones initially formed in the cycloaddition undergo dehydration under the reaction conditions. The reaction is regiospecific, and its direction is determined by polarization of the bonds in the starting enol and the aroyl ketenes. The yields of II–XI range from 6% to 41%; this is associated with the simultaneously occurring

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TABLE 1. Characteristics of the 2-Methyl- and 2-Methoxycarbonyl-3-acetyl-6-arylpyran-4-ones Obtained (II–XI)

Compound	Empirical formula	T_{mp}, °C	Yield, %
II	$C_{15}H_{14}O_3$	112...113	10
III	$C_{14}H_{14}ClO_3$	146...147	12
IV	$C_{15}H_{12}O_5$	126...127	11
V	$C_{15}H_{11}ClO_5$	165...167	21
VI	$C_{15}H_{11}BrO_5$	160...161	41
VII	$C_{20}H_{14}O_5$	234...236	34
VIII	$C_{21}H_{16}O_5$	209...210	32
IX	$C_{20}H_{13}ClO_5$	257...259	9
X	$C_{20}H_{13}BrO_5$	265...267	6
XI	$C_{20}H_{13}ClO_5$	225...226	20

dimerization of the aroyl ketenes to 6-aryl-3-aroyl-4-hydroxy-2-pyranones, as was previously noted in [1].

The IR spectra of II–XI contain absorption bands of carbonyl groups in the phenyl substituent (1682-1650 cm^{-1}), as well as an absorption band due to stretching vibrations of a C–H bond in the 5 position (3045-3080 cm^{-1}); this is in agreement with the literature data [5]. The spectra of IV–XI additionally contain an absorption band of an ester carbonyl group at 1730-1755 cm^{-1}.

In addition to multiplets of aromatic protons centered at 7.41-7.65 ppm (and signals of the methyl groups bonded with them in II and VIII), a singlet of a methylidyne proton in the 5 position of the heteroring at 6.65-7.35 ppm and a singlet of three protons of a methoxy group at 3.75-3.91 ppm for IV–XI and a methyl group in the 2 position of the heteroring at 2.28-2.45 ppm (for II and III) are observed in the PMR spectra of II–XI.

In the UV spectra of II and III λ_{max} is located at ∿268 nm (log ε 4.38); this is in agreement with the literature data [5]. In the case of IV–VI this maximum is shifted bathochromically to 282-286 nm (log ε 4.19-4.34). As a result of conjugation of the phenyl substituent with the pyranone ring in VII–XI a stronger bathochromic shift of the long-wave absorption maximum to 286-294 nm (log ε 4.10-4.18) occurs. The mass spectrum of VII contains peaks of molecular (m/z 334) and $[M - COOCH_3]^+$ (275) and $[M - COPh]^+$ (229) fragment ions; this is similar to the fragmentation of 3-acetyl-2-methyl-6-phenylpyran-4-one [5].

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil were obtained with a UR-20 spectrometer. The UV spectra of solutions in alcohol (10^{-5}-10^{-3} mmole/liter) were obtained with a Specord UV-vis spectrophotometer. The PMR spectra were recorded with an RS-60 spectrometer in d_6-DMSO with hexamethyldisiloxane (HMDS) as the internal standard. The mass spectrum was recorded with a Varian MAT-311A spectrometer. The results of elementary analysis for C, H, and Hal were in agreement with the calculated values.

6-Aryl-3-acetyl-2-methoxycarbonylpyran-4-ones IV–VI. A mixture of 1 mmole of dioxinone I and 1 mmole of methyl acetyl-pyruvate was heated at 130-140°C for 30 min, after which the cooled reaction mass was dissolved in 5-7 ml of ethanol, and the precipitated crystals were removed by filtration and recrystallized from ethanol.

2-Methyl- and 2-Methoxycarbonyl-6-aryl-3-acylpyran-4-ones II, III, and VII–XI. A mixture of 1 mmole of dioxinone I and 1.5 mmole of acetylacetone (in the case of II and III) or 1 mmole of methyl aroylpyruvate (in the case of VII–XI) was refluxed in 15-30 ml of dry xylene for 30 min, after which the mixture was stored in a refrigerator for 24 h. The precipitated crystals were removed by filtration and purified by recrystallization from ethanol (in the case of II, III, VII, and VIII), from CCl_4 (in the case of IX), or from toluene (in the case of X and XI).

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DECARBOXYLATION IN PROTON ACCEPTOR SOLVENTS

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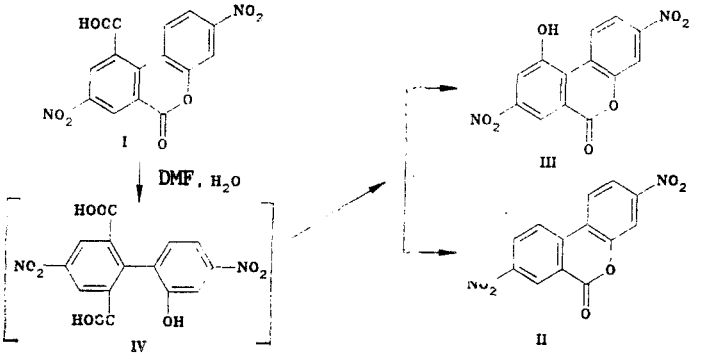
Heating 3,8-dinitro-10-carboxy-6H-dibenzo[b,d]pyran-6-one in DMSO, DMF, or HMPTA leads to decarboxylation and the replacement of the carboxyl group by a hydroxy group with the formation of 3,8-dinitro-6H-dibenzo[b,d]pyran-6-one and 3,8-dinitro-10-hydroxy-6H-dibenzo[b,d]pyran-6-one. The decarboxylation of 2,7-dinitro-5,10-dioxo-4,5,9,10-tetrahydro-4,9-dioxapyrene in HMPTA is preceded by opening of the two lactone rings and the formation of a 1:4 molecular complex of 4,4'-dinitro-6,6'-dihydroxy-2,2'-dicarboxybiphenyl with HMPTA, whose structure was established by x-ray diffraction structural analysis.

In previous work [1], we showed that heating 3,8-dinitro-10-carboxy-6H-dibenzo[b,d]-pyran-6-one (I) in DMSO or DMF at reflux leads to decarboxylation and the replacement of the carboxyl group by a hydroxy group with the formation of 3,8-dinitro-6H-dibenzo[b,d]pyran-6-one (II) and 3,8-dinitro-10-hydroxy-6H-dibenzo[b,d]pyran-6-one (III).



A mixture of lactone I and acid IV, which may be seen as an intermediate, was isolated upon the slow evaporation of a solution of I in DMF at room temperature. In HMPTA, which is also a strong proton acceptor solvent, I undergoes ring opening almost immediately after entering solution by adding a water molecule with the formation of a 1:3 complex of hydroxy-acid IV with HMPTA. The same products are formed upon heating a solution of lactone I in HMPTA as upon heating in DMSO and DMF, namely, II and III.

The possibility of such reactions for other compounds containing lactone rings was indicated by the decarboxylation of 2,7-dinitro-5,10-dioxo-4,5,9,10-tetrahydro-4,9-dioxapyrene (V) synthesized according to our previous procedure [2]. Heating V in HMPTA at 100°C for 5 h gives decarboxylation product III in 63% yield. The two lactone rings in V are initially opened with the formation of a 1:4 molecular complex of 4,4'-dinitro-6,6'-dihydroxy-2,2'-dicarboxybiphenyl (DNCB) with HMPTA (VI) and then one carboxyl group is lost. Product III is readily acetylated by acetic anhydride with the formation of 3,8-dinitro-10-acetoxy-6H-dibenzo[b,d]pyran-6-one (VII).

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