

Chemistry of 2-Methylene-2,3-dihydrofuran-3-ones: XVIII.* Reaction of Oxalyl Chloride with Acetophenone and Dibenzoylmethane

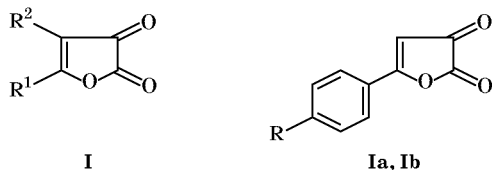
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Abstract—Treatment of acetophenone and dibenzoylmethane with excess oxalyl chloride gave heterocyclization products, 2-(3-oxo-5-phenyl-2,3-dihydrofuran-2-ylidene)-5-phenyl-2,3-dihydrofuran-3-one and a mixture of 4-benzoyl-5-phenyl-2,3-dihydrofuran-2,3-dione with 4-benzoyl-2-dibenzoylmethylene-5-phenyl-2,3-dihydrofuran-3-one.

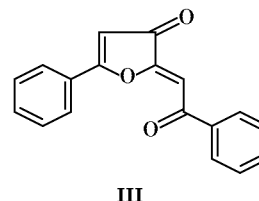
Trimethylsilyl enol ethers derived from methyl ketones and some β -diketones are known to react with oxalyl chloride to give substituted 2,3-dihydrofuran-2,3-diones **I** [2–6]. Sychev [7] briefly reported on the synthesis of 5-*p*-halophenyl-2,3-dihydrofuran-2,3-diones **Ia** and **Ib** in poor yields (22% and 43%) by keeping a mixture of *para*-substituted acetophenones with oxalyl chloride in hexane for several days.



I, R¹ = Alk, Ar; R² = H, Alk, Ph, COAlk, COPh, COOAlk;
Ia, R = Br; **Ib**, R = Cl.

We made an attempt to obtain 5-phenyl-2,3-dihydrofuran-2,3-dione (**Ic**) by the action of excess oxalyl chloride on acetophenone for a long time at room temperature. Surprisingly, we isolated in poor yield a dark brown condensation product, 2-(3-oxo-5-phenyl-2,3-dihydrofuran-2-ylidene)-5-phenyl-2,3-dihydrofuran-3-one (**II**) (Scheme 1), which can be regarded as a nonbenzoid oxa analog of Indigo. We failed to isolate the desired 2,3-furandione **Ic** from the reaction mixture, although during the first 24 h

we observed appearance and increase in intensity of yellow–orange color which could be ascribed to initially formed compound **Ic** or Knoevenagel condensation product of **Ic** with acetophenone, 2-benzoyl-methylene-5-phenyl-2,3-dihydrofuran-3-one (**III**):

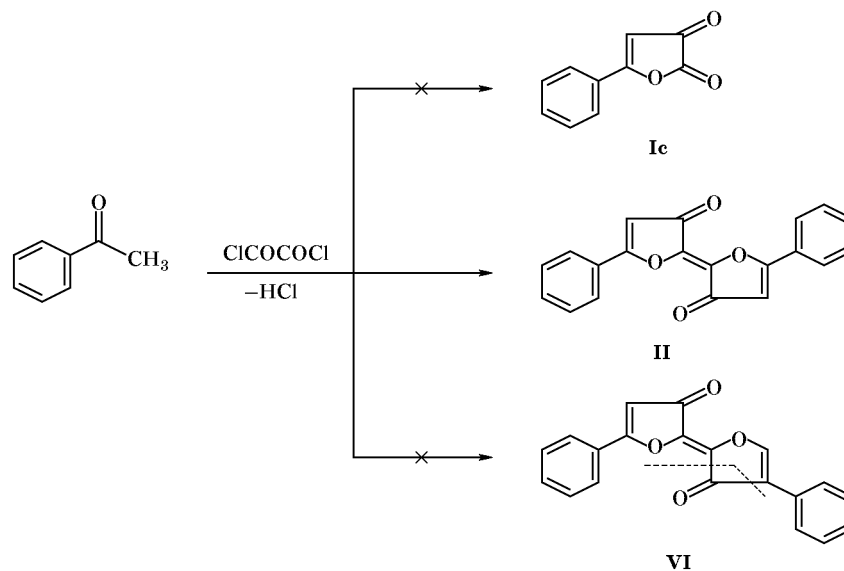


The possibility for Knoevenagel condensation of compound **Ic** with acetophenone under the given conditions follows from the results of heterocyclization of phenyl benzyl ketone by the action of oxalyl chloride, which leads to formation of 4,5-diphenyl-2-[benzoyl(phenyl)methylene]-2,3-dihydrofuran-3-one (**IV**) [8, 9] (Scheme 2). However, we previously found that 5-aryl-2,3-dihydrofuran-2,3-diones readily react with carbonyl compounds containing an active methylene group, following the Knoevenagel condensation pattern, but the products are stable cyclic semiacetals, 2-hydroxy-2,3-dihydrofuran-3-ones **V**, rather than 2-acylmethylene derivatives of 2,3-dihydrofuran-3-ones [10, 11] (Scheme 3).

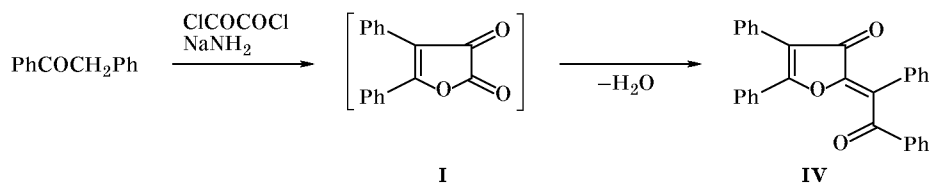
We failed to obtain compound **III** by independent synthesis, by the Wittig reaction of 2,3-furandione **Ia** with benzoylmethylene(triphenyl)phosphorane (the

* For communication XVII, see [1].

Scheme 1.

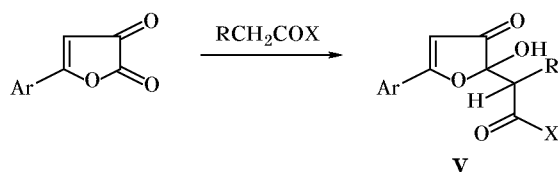


Scheme 2.



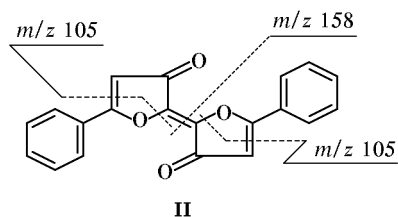
reaction resulted in complete tarring) [12], although analogous compounds with a halogen atom in the *para*-position of the phenacylidene fragment are accessible.

Scheme 3.



R = H, CN, CONH₂; X = Ar, OEt.

The structure of bis-furanone **II** was proved by spectral data. In the mass spectrum of **II** we observed



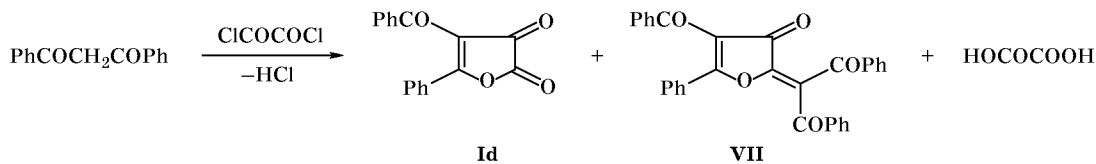
a fragment ion peak with m/z 158 corresponding to $[M/2]^+$. No ion with m/z 272 $[M-CO_2]^+$ was detected; therefore, an alternative lactone structure of 2-(2-oxo-5-phenyl-2,3-dihydrofuran-3-ylidene)-5-phenyl-2,3-dihydrofuran-3-one (**VI**) can be ruled out.

By the action of excess oxalyl chloride on dibenzoylmethane we obtained known 4-benzoyl-5-phenyl-2,3-dihydrofuran-2,3-dione (**Id**) (Ziegler's furandione) [2, 5, 6] and the Knoevenagel condensation product of **Id** with dibenzoylmethane, bright yellow 4-benzoyl-2-dibenzoylmethylene-5-phenyl-2,3-dihydrofuran-3-one (**VII**) (Scheme 4). The ¹H NMR spectrum of **VII** provides little information on its structure, for only aromatic proton signals were observed. Like other 2-acylmethylene-2,3-dihydrofuran-3-ones [12], compounds **II** and **VII** give rise to a dark red color on treatment with 10% alcoholic alkali.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 spectrometer in mineral oil. The ¹H NMR spectra were obtained on RYa-2310 (60 MHz) and Varian VXP-300 (300 MHz) instruments using DMSO-*d*₆

Scheme 4.



or CDCl_3 as solvent and TMS or HMDS as internal reference. The mass spectrum of **II** was measured on a Kratos MS-30 instrument (direct sample admission into the ion source, emission current 1000 mA, energy of ionizing electrons 70 eV, vaporizer temperature 120°C). The purity of the products was checked by TLC on Silufol UV-254 plates using benzene–diethyl ether–acetone (10:9:1) as eluent; development with iodine vapor. The constants of 4-benzoyl-5-phenyl-2,3-dihydrofuran-2,3-dione (**Id**) coincided with those reported in [2].

2-(3-Oxo-5-phenyl-2,3-dihydrofuran-2-ylidene)-5-phenyl-2,3-dihydrofuran-3-one (II). Oxalyl chloride, 10 ml (6-fold excess), was carefully added with stirring to 2.40 g (0.02 mol) of acetophenone, and the mixture was kept for 20 days at room temperature. The dark brown needles were filtered off and washed with ether. Yield 0.05 g (1.6%). mp 270°C (decomp.). IR spectrum, ν , cm^{-1} : 1748 ($\text{C}^3=\text{O}$), 1698 ($\text{C}^2=\text{C}^2'$). ^1H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 4.75 s (2H, 2CH), 7.40–7.95 m (10H, $2\text{C}_6\text{H}_5$). Mass spectrum, m/z (I_{rel} , %; peaks with $I > 2\%$ are given): 317 (5) $[M+1]^+$, 316 (28) $[M]^+$, 288 (2) $[M-\text{CO}]^+$, 270 (2), 260 (2) $[M-2\text{CO}]^+$, 244 (2), 226 (2), 211 (2), 202 (2), 193 (2), 171 (2), 158 (5) $[M/2]^+$, 139 (3), 122 (2), 106 (7), 105 (100) $[\text{PhCO}]^+$, 87 (3), 77 (65) $[\text{C}_6\text{H}_5]^+$, 69 (2) $[\text{OCCHCO}]^+$, 51 (18). Found, %: C 76.29; H 3.65. $\text{C}_{20}\text{H}_{12}\text{O}_4$. Calculated, %: C 75.94; H 3.82.

Reaction of dibenzoylmethane with oxalyl chloride. Oxalyl chloride, 20 ml (twofold excess), was added with stirring at room temperature to a solution of 18.0 g (0.08 mol) of dibenzoylmethane in 100 ml of dry diethyl ether. The originally colorless mixture gradually turned lemon yellow. The mixture was kept for 10–15 h, and the yellow precipitate of 4-benzoyl-5-phenyl-2,3-dihydrofuran-2,3-dione (**Id**) was filtered off and washed with dry diethyl ether. The filtrate was evaporated, and the thick brown residue was treated with 200 ml of water. We thus isolated the second yellow crystalline product, 4-benzoyl-2-dibenzoylmethylene-5-phenyl-2,3-dihydrofuran-3-one (**VII**).

Compound **Id**. Yield 5.0 g (67%). mp $133\text{--}134^\circ\text{C}$ (decomp.) [2]. $\text{C}_{17}\text{H}_{10}\text{O}_4$. M 278.26.

Compound **VII**. Yield 10.0 g (77%). mp $139\text{--}140^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 1664, 1638 ($\text{C}=\text{O}$, $\text{C}=\text{C}$); 1604, 1576 ($\text{C}=\text{C}_{\text{arom}}$). ^1H NMR spectrum (CDCl_3), δ , ppm: 7.04–8.02 m (20H, $4\text{C}_6\text{H}_5$). Found, %: C 80.67; H 4.02. $\text{C}_{32}\text{H}_{20}\text{O}_5$. Calculated, %: C 79.33; H 4.16.

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