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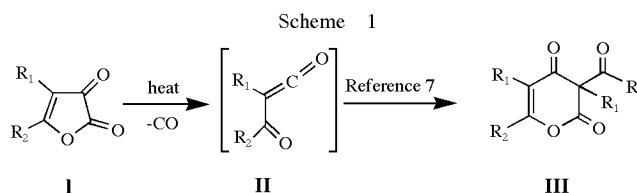
4-Ethoxycarbonyl-5-phenyl-2,3-dihydrofuran-2,3-dione **1** reacts with aldehydes *via* the acylketene intermediate **2** giving the 1,3-dioxin-4-ones **3a-e** and the 1,4-bis(5-ethoxycarbonyl-4-oxo-6-phenyl-4*H*-1,3-dioxin-2-yl)benzene **4**, and a one step reaction between dibenzoylmethane and oxalylchloride gave 3,5-dibenzoyl-2,6-diphenyl-4-pyrone **7**. The reaction of **1** with dibenzoylmethane, a dicarbonyl compound, provided ethyl 3-benzoyl-4-oxo-2,6-diphenylpyran-5-carboxylate derivative **9**. Compound **9** was converted into the corresponding ethyl 3-benzoyl-4-hydroxy-2,6-diphenylpyridine-5-carboxylate derivative **10** *via* its reaction with ammonium hydroxide solution in 1-butanol.

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α -Oxoketenes (acyl ketenes) are highly reactive molecules which usually cannot be isolated under ordinary reaction conditions, although several examples have been detected by low-temperature ir spectroscopy technique [1], and some sterically or electronically-hindered α -oxoketenes have been stabilized by preparative flash vacuum pyrolysis method in recent years [2]. These ketenes are currently of considerable interest, not only because of mechanistic and theoretical considerations [3], but also because of their use as synthetic building blocks in organic synthesis [2,4].

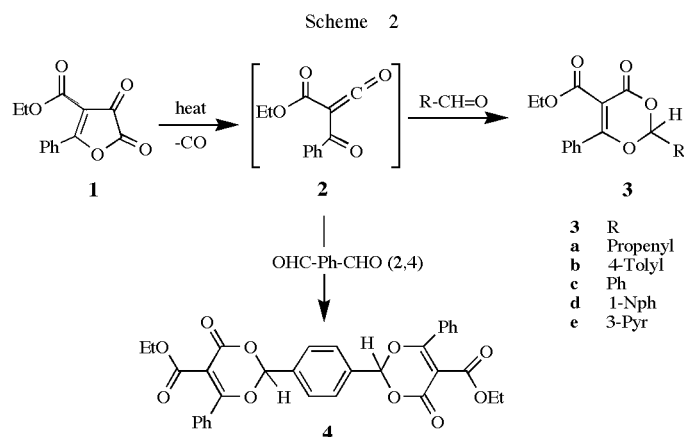
A simple useful procedure of the generation of α -oxoketenes **II** is the thermal decomposition of 2,3-dihydrofuran-2,3-diones **I** in solution [4,5]. Elevated temperature leads to the thermal decomposition of furandiones **I** with the loss of CO to give the corresponding α -oxoketenes intermediates **II** [7]. Typically, reactive ketene **II** is generated *in situ* from furandione at approximately 80-130 °C, and is trapped immediately with nucleophiles [5], or in [2+4] cycloaddition reactions with heterodienophiles having double or triple polar bonds [6]. If there is not any heterodienophile or nucleophile in reaction medium, it is well known that all acyl and diacyl ketenes (α -oxoketenes) undergo dimerization which proceeds *via* [2+4] cycloaddition of one α -oxoketene molecule to the C=C bond of another to give 2,4-pyrandiones **III** [8]. In the case of the presence of a carbonyl compound or another heterodienophile such as a Schiff base, a nitrile, or isocyanate, the [2+4] cycloaddition reaction now involves one molecule of α -oxoketene as a component with four electrons being added to the one of C=O, C=N, C≡N or N=C=O groups of heterodienophiles, to give various dioxinone, oxazinone, and oxazindione derivatives [6,7,9], respectively (Scheme 1).

In this study we envisioned that we could generate α -oxoketene from 4-ethoxycarbonyl-5-phenyl-2,3-dihydrofuran-2,3-dione **1** which was obtained by the cyclocondensation reaction between ethylbenzoylacetate and oxalylchloride [6], and trap it in [2+4] cycloaddition reactions with some carbonyl compounds.



4-Ethoxycarbonyl-5-phenyl-2,3-dihydrofuran-2,3-dione **1** reacts easily with aldehydes *via* the ethoxycarbonylbenzoylketene intermediate **2** yielding the 1,3-dioxin-4-one derivatives **3** in moderate yields.

The reaction between **1** and aldehydes was realized in boiling benzene (80 °C). During this type of reactions, due to reason mentioned above, side reactions, such as dimerization of α -oxoketenes may occur, which can also explain moderate yields of cycloadduct obtained in this work. Consequently, α -oxoketene **2** generated *in situ* from **1** in boiling benzene showed a pronounced tendency to form [2+4] Diels-Alder adduct when trapped by aldehydes that behave as a heterodienophile in these reactions. The structures of 1,3-dioxinone derivatives **3** and **4** obtained in this way were confirmed by analytical and spectral data (see experimental). In the ir spectra, the presence of C=O absorption bands at approximately

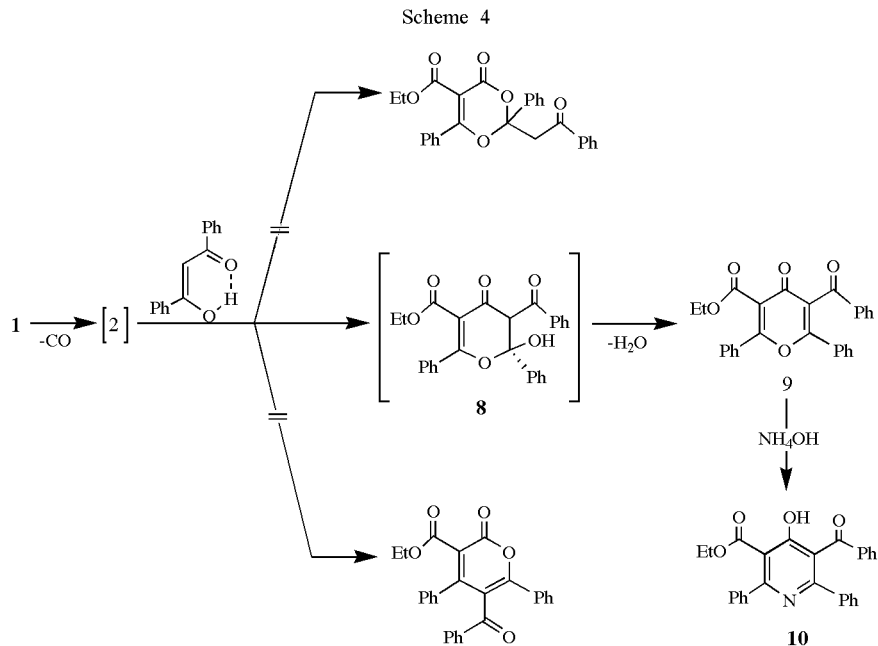
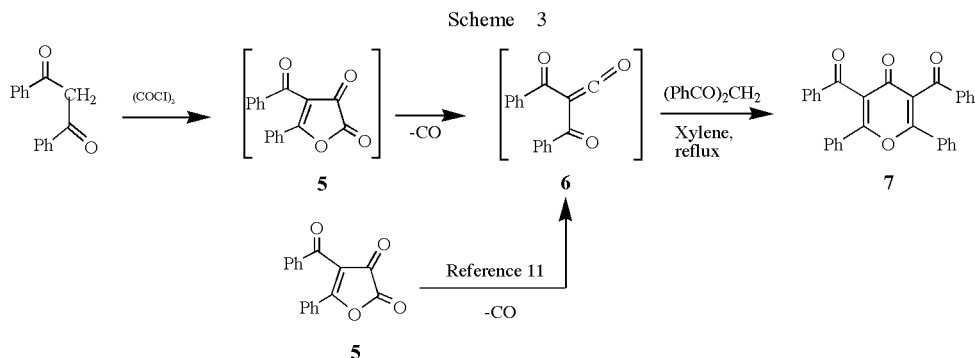


1750-1720 cm^{-1} besides the absence of OH vibration bands is characteristic for 1,3-dioxin-4-ones [10]. ^1H -nmr spectrum exhibits a singlet at $\delta=6.05\text{--}7.46$ ppm for aldehyde adducts (Scheme 2).

In our previous research, we demonstrated that dibenzoylketene **6** generated *in situ* from 4-benzoyl-5-phenyl-2,3-dihydrofuran-2,3-dione **5** in refluxing xylene, has reacted easily with dibenzoylmethane to give 3,5-dibenzoyl-2,6-diphenyl-4-pyrone derivative **7** [11] in higher yield than that reported in the literature [12]. In this study, the same pyrone compound has been obtained again in one step reaction between dibenzoylmethane and oxalylchloride (Scheme 3).

addition, compound **9** could be easily converted *via* its reactions with ammoniumhydroxyde solution in 1-butanol into the corresponding pyridine derivative **10**, structure of which was also elucidated by elemental analysis and spectroscopic data (Scheme 4).

The formation of **9** (or **7**) is probably occurring *via* [2+4] cycloaddition of α -oxoketene intermediates **2** (or **6**) to C=C bond of cyclic enol form of dibenzoylmethane and elimination of water in the final step affording pyrone nucleus similar to the cycloaddition of α -oxoketenes to vinyl ethers [2b]. Nucleophilic attack of OH group in enol form of dibenzoylmethane and cycloaddition of carbonyl group of dibenzoylmethane to ketene group of



On the other hand, the reaction of **1** with dibenzoylmethane, which is a 1,3-dicarbonyl compound instead of aldehyde did not lead to the corresponding 1,3-dioxinone derivative. When dibenzoylmethane was added to **2** generated from **1**, a new γ -pyrone derivative **9** was obtained. In

α -oxoketene intermediates **2** (or **6**) would lead to the formation of compounds different than the γ -pyrone derivatives **9** (or **7**) (Scheme 3 and 4). Additionally, nucleophilic attacks of OH group at the furan ring carbon atoms in **5** could convert furandione **5** into starting materials; these

materials are dibenzoylmethane and oxalic acid derivatives [13]. From these reactions in Scheme 3 and 4, it may be deduced that dibenzoylmethane is found in the cyclic enol form having a strong intramolecular hydrogen bond in boiling xylene, therefore its OH group cannot react with furandiones of type **1** or **5**.

The structures of compounds **3a-e**, **4-10** and **7** were confirmed by analytical and spectral data (see experimental).

EXPERIMENTAL

Solvents were dried by refluxing with the appropriate drying agents and distilled before use. Melting points were determined on an Electrothermal Gallenkamp apparatus and are uncorrected. Microanalyses were performed on a Carlo Erba Elemental Analyser Model 1108. The IR spectra were obtained as potassium bromide pellets using a Mattson 1000 FTIR spectrometer. The ^1H and ^{13}C -nmr spectra were recorded on Varian (200 MHz) and Varian (50 MHz) spectrometers, respectively, using TMS as an internal standard. All experiments were followed by the using DC Alufolien Kieselgel 60 F 254 Merc and Camag tlc lamp (254/366 nm).

Ethyl 4-Oxo-6-phenyl-2-propenyl-4*H*-1,3-dioxine-5-carboxylate (**3a**).

General Procedure.

A milliequimolar mixture of **1** (0.246 g, 1 mmol) and crotonaldehyde (0.07 g, 1 mmol) was refluxed in benzene (20 ml) for 6 h. After the solvent was removed by evaporation, the oily residue was treated with ether for 4 h., with stirring. The formed crude product was crystallized from ethanol to give 0.153 g (53%) of **3a**; mp 120 °C; ir: 3076 cm^{-1} (Ar-H), 2987-2906 cm^{-1} (R-H), 1757, 1715 cm^{-1} (C=O); ^1H -nmr (200 MHz, deuteriochloroform): δ 1.09 (t, 3H, CH_3 , ethyl), 1.87 (d, 3H, CH_3 , propenyl), 4.16 (m, 2H, O- CH_2), 5.83 (d.d, 1H, H-1'), 6.05 (d, 1H, H-2), 6.25 (m, 1H, H-2'), 7.26-7.63 ppm (m, 5H, Ar-H).

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_5$: C, 66.66; H, 5.59. Found: C, 66.48; H, 5.58.

Ethyl 4-Oxo-6-phenyl-2-*p*-tolyl-4*H*-1,3-dioxine-5-carboxylate (**3b**).

Compound **3b** was prepared according to the general procedure above with a reflux time of 5 hours (4-methylbenzaldehyde) resulting in 55 % yield (0.186 g); mp 138 °C (Ethanol); ir: 3000-3050 cm^{-1} (Ar-H), 2960- 2875 cm^{-1} (R-H); 1746, 1705 cm^{-1} (C=O); ^1H -nmr (200 MHz, deuteriochloroform): δ 1.12 (t, 3H, CH_3 , ethyl), 2.41 (s, 3H, CH_3), 4.17 (m, 2H, O- CH_2), 6.61 (s, 1H, H-2), 7.26- 7.67 ppm (m, 9H, Ar- H).

Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_5$: C, 70.99; H, 5.36. Found: C, 70.81; H, 5.34.

Ethyl 4-Oxo-2,6-diphenyl-4*H*-1,3-dioxine-5-carboxylate (**3c**).

Compound **3c** was prepared according to the general procedure above with a reflux time of 7 hours (benzaldehyde) resulting in 64 % yield (0.207 g); mp 145 °C (1-propanol); ir: 3073-3043 cm^{-1} (Ar- H), 2979-2874 cm^{-1} (R-H), 1757,1704 cm^{-1} (C=O); ^1H -nmr (200 MHz, deuteriochloroform): δ 1.10 (t, 3H, CH_3), 4.18 (m, 2H, O- CH_2), 6.63 (s, 1H, H-2), 7.38-7.66 ppm (m, 10H, Ar-H); ^{13}C -nmr (50 MHz, deuteriochloroform): δ 15.66 (CH_3), 63.68 (O- CH_2), 102.14 (C-2), 106.29 (C-5), 128.71,130.57,

130.73, 130.97, 132.61, 132.69, 134.73, 135.00, 161.47 (C-6), 165.68, (C=O, ester),172.61 ppm (C=O, C-4).

Anal. Calcd. for $\text{C}_{19}\text{H}_{16}\text{O}_5$: C, 70.36; H, 4.97. Found: C, 70.51; H, 4.96.

Ethyl 2-Naphth-1-yl-4-oxo-6-phenyl-4*H*-1,3-dioxine-5-carboxylate (**3d**).

Compound **3d** was prepared according to the general procedure above with a reflux time of 5 hours (1-naphthaldehyde) resulting in 65 % yield (0.243 g); mp 164 °C (anhydrous acetic acid); ir: 3097-3008 cm^{-1} (Ar-H), 2938-2850 cm^{-1} (R-H), 1745, 1697 cm^{-1} (C=O); ^1H -nmr (200 MHz, deuteriochloroform): δ 1.05 (t, 3H, CH_3), 4.15 (m, 2H, O- CH_2), 7.37 (s, 1H, H-2), 7.51-8.42 ppm (m, 12H, Ar-H).

Anal. Calcd. for $\text{C}_{23}\text{H}_{18}\text{O}_5$: C, 73.79; H, 4.85. Found: C, 73.54; H, 4.84.

Ethyl 4-Oxo-6-phenyl-2-pyridin-3-yl-4*H*-1,3-dioxine-5-carboxylate (**3e**).

Compound **3e** was prepared according to the general procedure above with a reflux time of 6 hours (3-pyridine carbaldehyde) resulting in 60 % yield (0.195 g); mp 165 °C (ethanol); ir: 3150-3075 cm^{-1} (Ar-H), 2975-2890 cm^{-1} (R-H), 1735 cm^{-1} , 1723 cm^{-1} (C=O); ^1H -nmr (200 MHz, deuteriochloroform): δ 1.13 (t, 3H, CH_3), 4.21 (m, 2H, O- CH_2), 6.73 (s, 1H, H-2), 7.27-8.9 ppm (m, 9H, Ar-H); ^{13}C -nmr (50 MHz, deuteriochloroform): δ 15.67 (CH_3), 63.91 (O- CH_2), 100.35 (C-2), 106.51 (C-5), 125.57, 125.59, 130.70, 131.00, 132.21, 135.04, 136.41, 150.18 (C-2' or C-6', pyr), 153.92 (C-2' or C-6', pyr), 160.91 (C-6), 165.44 (C=O, ester), 172.95 ppm (C=O).

Anal. Calcd. for $\text{C}_{18}\text{H}_{15}\text{NO}_5$: C, 66.46; H, 4.65; N, 4.31. Found: C, 66.68; H, 4.64; N, 4.30.

1,4-Bis(5-ethoxycarbonyl-4-oxo-6-phenyl-4*H*-1,3-dioxin-2-yl)-benzene (**4**).

This compound was obtained from **1** and terephthaldicarboxaldehyde (molar ratio 2:1), according to the general procedure above with a reflux time of 7 hours resulting in 55 % yield (0.314 g); m.p 178 °C (anhydrous acetic acid); ir: 3085 cm^{-1} (Ar-H), 2981, 2900 cm^{-1} (R-H), 1761, 1708 cm^{-1} (C=O); ^1H -nmr (200 MHz, deuteriochloroform): δ 1.03 (t, 6H, CH_3), 4.12 (m, 4H, O CH_2), 7.46 (s, 2H, H-2), 7.50-7.98 ppm (m, 14H, Ar-H).

Anal. Calcd. for $\text{C}_{32}\text{H}_{26}\text{O}_{10}$: C, 67.36; H, 4.59. Found: C, 67.20; H, 4.58.

3,5-Dibenzoyl-2,6-diphenyl-4-pyrone (**7**).

A milliequimolar solution of dibenzoylmethane (0.224 g, 1 mmol) and oxalylchloride (0.122 ml, 1 mmol) in xylene (20 ml) was refluxed for about 15 minutes until the solution became yellow color. After the addition of the remaining dibenzoylmethane (0.224 g, 1 mmol) to the reaction mixture, the solution was refluxed again for 2.5 hours until the appearance of white precipitates. Subsequent to cooling at room temperature, the formed precipitate was collected by filtration and recrystallized from 1-butanol to give 0.296 g (65 %) of **7**. m.p 280 °C (Lit. mp 280 °C); ir: 3106-3000 cm^{-1} (Ar-H), 1702,1651 cm^{-1} (C=O), 1625 cm^{-1} (C=C, pyrone); ^1H -nmr (200 MHz, deuteriochloroform): δ 8.10-7.42 ppm (Ar-H); ^{13}C -nmr (50 MHz, deuteriochloroform): δ 127.05, 130.07, 130.68, 130.79, 131.00, 132.73, 133.34, 136.06, 138.06, 163.72 (C-2 and C-6), 177.56 (C=O, C-4), 194.28 ppm (C=O, benzoyl).

Anal. Calcd. for $C_{31}H_{20}O_4$: C, 81.56; H, 4.42. Found: C, 81.38; H, 4.41.

Ethyl 3-Benzoyl-2,6-diphenyl-4-pyrone-5-carboxylate (**9**).

A miliequimolar mixture of **1** (0.246 g, 1 mmol) and dibenzoylmethane (0.224 g, 1 mmol) was refluxed in xylene (20 ml) for about 2 hours until the appearance of white crystals. After cooling at room temperature, the formed crystals were collected by filtration and recrystallized from 1-butanol to give 0.326 g (77 %) of **5** mp 197 °C; ir: 3080-3060 cm^{-1} (Ar-H), 2950-2850 cm^{-1} (R-H), 1736, 1677, 1641 cm^{-1} (C=O), 1620 cm^{-1} (C=C, pyrone); 1H -nmr (200 MHz, deuteriochloroform): δ 1.17 (t, 3H, CH_3), 4.26 (q, 2H, O- CH_2), 7.29-7.95 ppm (m, 15H, Ar-H); ^{13}C -nmr (50 MHz, deuteriochloroform): δ 15.80 (CH_3), 64.00 (O- CH_2), 123.75 (C-3 or C-5), 128.03 (C-3 or C-5), 129.92, 130.22, 130.77, 130.86, 130.93, 131.32, 132.77, 133.02, 133.56, 133.81, 135.86, 138.72, 163.79 (C-2 or C-6), 164.51 (C-2 or C-6), 166.06 (C=O, ester), 176.40 (C=O, C-4), 194.21 ppm (C=O, benzoyl)

Anal. Calcd. for $C_{27}H_{20}O_5$: C, 76.40; H, 4.75. Found: C, 76.65; H, 4.74.

Ethyl 3-Benzoyl-2,6-diphenyl-4-hydroxypyridine-5-carboxylate (**10**).

To the solution of **9** (0.456 g, 1 mmol) in 1-butanol (25 ml) was added a slight excess of saturated aqueous solution of ammoniumhydroxyde with stirring. Then the reaction mixture was refluxed for 4 hours. After the solvents were removed by evaporation, the oily residue was treated with ether and the formed crude product was crystallized from methanol to give 0.220 g (52 %) of **10** m.p 297 °C; ir: 3100-3015 cm^{-1} (Ar-H), 2985-2875 cm^{-1} (R-H), 1745 cm^{-1} , 1695 cm^{-1} , 1655 cm^{-1} (C=O); 1H -nmr (200 MHz, deuteriochloroform): δ 0.92 (t, 3H, CH_3), 4.13 (q, 2H, O- CH_2), 7.22-7.85 ppm (m, 15H, Ar-H); ^{13}C -nmr (50 MHz, deuteriochloroform): δ 15.18 (CH_3), 63.89 (O- CH_2), 114.63, 129.89, 130.00, 130.27, 130.53, 130.66, 130.79, 131.17, 131.31, 131.43, 135.49, 139.32, 140.20, 154.23 (C-2 or C-6), 157.91 (C-2 or C-6), 168.28 (ester), 171.75 (C=O, C-4), 197.23 ppm (C=O, benzoyl).

Anal. Calcd. for $C_{27}H_{21}NO_4$: C, 76.58; H, 5.00; N, 3.31. Found: C, 76.87; H, 4.98; N, 3.32.

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