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## One Step Synthesis of Some 2,5,6-Trisubstituted-1,3-Dioxin-4-ones

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A number of novel 2,5,6-trisubstituted-1,3-dioxin-4-one derivatives were synthesized via one step reactions between dibenzoylmethane or benzoylacetone and oxalyl chloride in refluxing solvents containing various aldehydes.

**Key Words:** Cyclic oxalyl compounds,  $\alpha$ -oxoketene, 1,3-dioxin-4-one

### Introduction

$\alpha$ -Oxoketenes (acylketenes) are highly reactive molecules that usually cannot be observed or isolated under ordinary reaction conditions, although several examples have been detected by low-temperature IR spectroscopy,<sup>1,2</sup> and some sterically or electronically hindered  $\alpha$ -oxoketenes have been stabilized by preparative flash vacuum pyrolysis in recent years.<sup>3-5</sup> These ketenes are currently of considerable interest, not only because of mechanistic and theoretical considerations,<sup>6</sup> but also because of their use as synthetic building blocks in organic synthesis.<sup>7-9</sup>

A simple useful procedure for the generation of  $\alpha$ -oxoketenes is the thermal decarbonylation of 2,3-furandiones in solution.<sup>10-13</sup> Typically, reactive ketenes are generated in situ from 2,3-furandiones at approximately 80-130 °C, and are trapped immediately with nucleophiles,<sup>10-13</sup> or in [2+4] cycloaddition reactions with heterodienophiles having double or triple polar bonds such as carbonyl, Schiff base, nitrile, isocyanate, ketene, ketimine and vinyl ether to give various dioxinone, oxazinone, oxazindione, pyrandione, and 4-pyrone derivatives.<sup>4,14-17</sup> In the absence of a heterodienophile or a nucleophile in the reaction medium, it is well known that all acyl and diacyl ketenes undergo dimerization, which proceeds via [2+4] cycloaddition of one  $\alpha$ -oxoketene molecule to the C=C bond of another to give 2,4-pyrandiones.<sup>18,19</sup> Our studies related

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to the preparation of some 2,3,5,6-tetrasubstituted-4-pyrone derivatives via cycloaddition reactions of  $\alpha$ -oxoketenes generated in situ by thermolysis of 2,3-furandiones formed during one step reactions of oxalyl chloride with some diketones in boiling xylene were previously reported.<sup>11,20</sup> Here, we attempted to extend our investigations on the trapping of  $\alpha$ -oxoketenes generated by one step reactions between dicarbonyl compounds and oxalyl chloride in [2+4] cycloaddition reactions with various aldehydes.

## Experimental

FT-IR spectra were recorded on a Perkin-Elmer 1710 FT spectrophotometer using KBr pellets. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were obtained on Varian spectrometers (200 MHz and 50 MHz respectively), using DMSO-*d*<sub>6</sub> as a solvent and TMS as an internal standard. Elemental analyses were performed on a Carlo Erba EAGER 200 microanalyzer. Melting points were determined on an Electrothermal Gallenkamp apparatus and not corrected. All reagents and solvents were obtained from commercial suppliers and were of reagent grade quality.

### 5-benzoyl-2,6-diphenyl-[1,3]dioxin-4-one (1a)

An equimolar mixture of dibenzoylmethane (0.22 g, 1 mmol) and oxalylchloride (0.09 mL, 1 mmol) was refluxed in anhydrous benzene containing a slight excess of benzaldehyde (0.15 mL, 1.5 mmol) for 8 h. After the solvent was removed by evaporation, the formed residue was crystallized from ethanol to give 0.23 g of **1a**. Yield 65%, mp 160-161 °C; FT-IR:  $\nu_{max}$  3044 (CH, aromatic), 1727 (C=O), 1660 cm<sup>-1</sup> (C=O, benzoyl); <sup>1</sup>H-NMR [DMSO-*d*<sub>6</sub>]:  $\delta$  8.01-7.22 ppm (m, Ar-H and H-2); <sup>13</sup>C-NMR [DMSO-*d*<sub>6</sub>]:  $\delta$  191.6, 168.9, 161.0, 137.3, 134.7, 134.1, 133.4, 131.3, 130.7, 130.1, 129.6, 129.5 (2 C), 127.6 (2 C), 109.3, 100.4 ppm; C<sub>23</sub>H<sub>16</sub>O<sub>4</sub> (356.37): Calcd C 77.52, H 4.53; Found C 77.01, H 4.51.

### 5-benzoyl-2-(3,4-dimethoxy-phenyl)-6-phenyl-[1,3]dioxin-4-one (1b)

Compound **1b** was prepared according to the procedure given for **1a** by the reaction of an equimolar mixture of dibenzoylmethane and oxalylchloride with 3,4-dimethoxybenzaldehyde with a reflux time of 8 h, resulting in 56% yield, mp 173-175 °C; FT-IR:  $\nu_{max}$  3060 (CH, aromatic), 2981 (CH, aliphatic), 1731 (C=O), 1662 cm<sup>-1</sup> (C=O, benzoyl); <sup>1</sup>H-NMR [DMSO-*d*<sub>6</sub>]:  $\delta$  8.17-7.34 (m, 9H, Ar-H), 7.33 [s, 1H, H-2' (MeO)<sub>2</sub>Ph or H-2], 7.30 (d, 1H, Ar-H), 7.24 (s, 1H, H-2' or H-2), 7.15 (d, 1H, H-5' or H-6'), 7.10 (d, 1H, H-5' or H-6'), 3.85 (s, 3H, CH<sub>3</sub>), 3.81 ppm (s, 3H, CH<sub>3</sub>); <sup>13</sup>C-NMR [DMSO-*d*<sub>6</sub>]:  $\delta$  191.6, 169.0, 161.3, 151.3, 149.5, 137.4, 135.2, 134.7, 133.7, 133.3, 130.8, 130.1, 129.6, 129.5, 128.1, 120.9, 112.1, 111.9, 100.7, 56.5, 56.3; C<sub>25</sub>H<sub>20</sub>O<sub>6</sub> (416.42): Calcd C 72.11, H 4.84; Found C 72.36, H 4.80.

### 5-benzoyl-2-naphthalen-1-yl-6-phenyl-[1,3]dioxin-4-one (1c)

Compound **1c** was prepared according to the procedure given for **1a** by the reaction of an equimolar mixture of dibenzoylmethane and oxalylchloride with 1-naphthaldehyde with a reflux time of 8 h, resulting in 43% yield, mp 165-166 °C; FT-IR:  $\nu_{max}$  3040 (CH, aromatic), 1731 (C=O), 1666 cm<sup>-1</sup> (C=O, benzoyl); <sup>1</sup>H-NMR [DMSO-*d*<sub>6</sub>]:  $\delta$  8.50-7.25 ppm (m, Ar-H and H-2); <sup>13</sup>C-NMR [DMSO-*d*<sub>6</sub>]:  $\delta$  191.7, 169.2, 161.2, 137.4, 134.7, 134.1, 133.3, 132.0, 130.8, 130.5, 130.3 (2 C), 129.58, 129.50, 129.3, 127.8 (2 C), 127.2, 127.1, 125.8, 124.9, 109.4, 100.1 ppm; C<sub>27</sub>H<sub>18</sub>O<sub>4</sub> (406.43): Calcd C 79.79, H 4.46; Found C 79.55, H 4.47.

### 1,4-Bis-(5-benzoyl-4-oxo-6-phenyl-4H-[1,3]dioxin-2-yl)-benzene (2)

An equimolar mixture of dibenzoylmethane (0.56 g, 2.5 mmol) and oxalylchloride (0.22 mL, 2.5 mmol) was refluxed in anhydrous benzene containing terephthalaldehyde (0.13 g, 1 mmol) for 8 h. After the solvent was removed by evaporation, the formed residue was crystallized from ethanol to give 0.22 g of **2**. Yield 35%, mp 217-218 °C; FT-IR:  $\nu_{max}$  3062 (CH, aromatic), 1719 (C=O), 1661  $\text{cm}^{-1}$  (C=O, benzoyl);  $^1\text{H-NMR}$  [DMSO- $d_6$ ]:  $\delta$  8.17-7.03 ppm (m, Ar-H and H-2);  $^{13}\text{C-NMR}$  [DMSO- $d_6$ ]:  $\delta$  191.5, 168.9, 160.8, 137.3, 136.4, 134.7, 133.5, 130.7, 130.1, 129.7, 129.5, 128.1 (2 C), 109.4, 100.0 ppm;  $\text{C}_{40}\text{H}_{26}\text{O}_8$  (634.63): Calcd C 75.70, H 4.13; Found C 75.46, H 4.16.

### 5-benzoyl-6-methyl-2-phenyl-[1,3]dioxin-4-one (3)

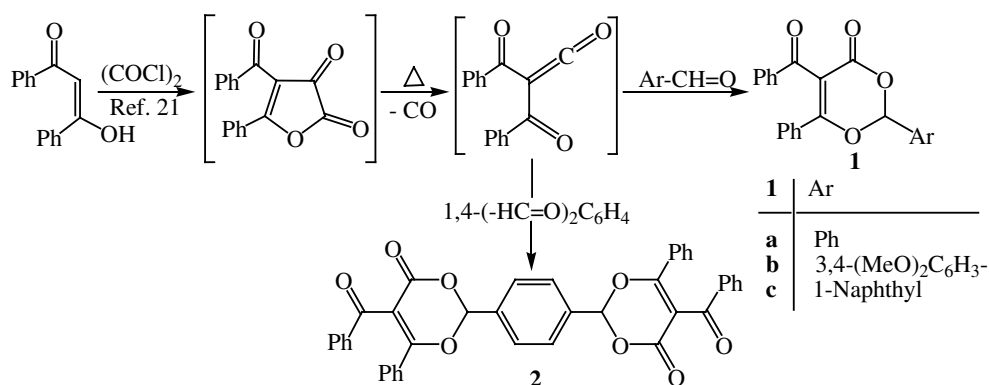
An equimolar mixture of benzoylacetone (0.16 g, 1 mmol) and oxalylchloride (0.09 mL, 1 mmol) was refluxed in xylene containing benzaldehyde (0.15 mL, 1.5 mmol) for 1 h. After evaporation of the solvent, the formed residue was crystallized from a mixture of n-hexane and ether (volume ratio, 1:2) to give 0.07 g of **3**. Yield 25%, mp 127-128 °C; FT-IR:  $\nu_{max}$  3044 (CH, aromatic), 2988 (CH, aliphatic), 1715 (C=O), 1665  $\text{cm}^{-1}$  (C=O, benzoyl);  $^1\text{H-NMR}$  [DMSO- $d_6$ ]:  $\delta$  7.97-7.51 (m, 10H, Ar-H), 7.14 (s, 1H, H-2), 2.47 ppm (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C-NMR}$  [DMSO- $d_6$ ]:  $\delta$  191.6, 175.0, 161.1, 137.9, 134.4, 133.9, 131.4, 129.9, 129.49, 129.41, 127.5, 110.0, 100.1, 18.8 ppm;  $\text{C}_{18}\text{H}_{14}\text{O}_4$  (294.30): Calcd C 73.46, H 4.79; Found C 73.35, H 4.81.

### 1,4-Bis-(5-benzoyl-6-methyl-4-oxo-4H-[1,3]dioxin-2-yl)-benzene (4)

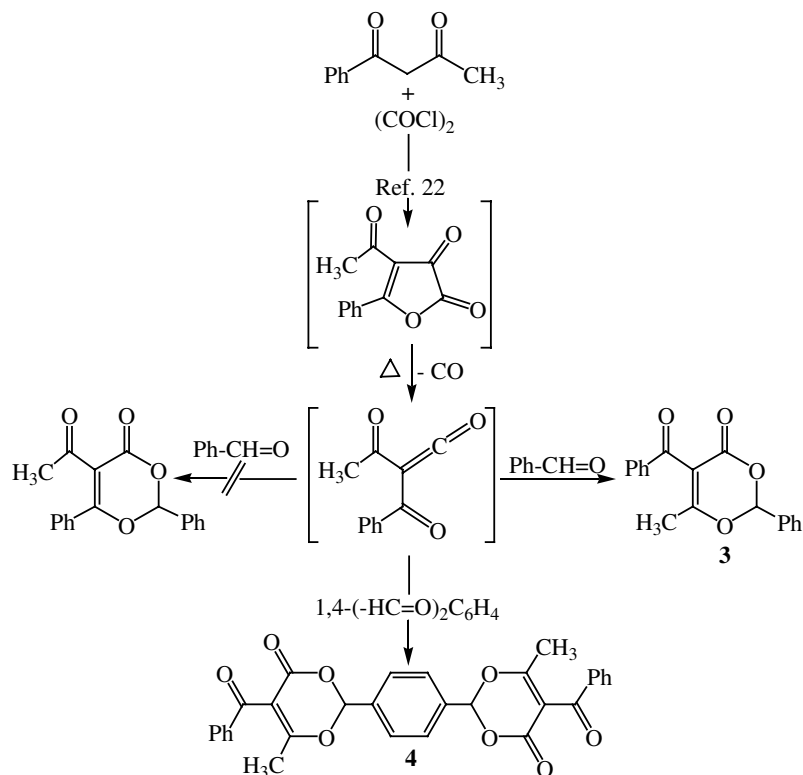
Benzoylacetone (0.41 g, 2.5 mmol) and oxalylchloride (0.22 mL, 2.5 mmol) were refluxed in xylene containing terephthalaldehyde (0.13 g, 1 mmol) for about 40 min until the appearance of white crystals. After cooling at room temperature, the formed crystals were collected by filtration and washed with boiling xylene to give 0.32 g of **4**. Yield 63%, mp 213-215 °C; FT-IR:  $\nu_{max}$  3063 (CH, aromatic), 2916 (CH, aliphatic), 1721 (C=O), 1658  $\text{cm}^{-1}$  (C=O, benzoyl);  $^1\text{H-NMR}$  [DMSO- $d_6$ ]:  $\delta$  8.08-7.52 (m, 7H, Ar-H), 7.23 (s, 1H, H-2), 2.20 ppm (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C-NMR}$  [DMSO- $d_6$ ]:  $\delta$  191.5, 174.9, 160.8, 137.8, 136.2, 134.5, 129.9, 129.4, 128.0, 110.1, 100.0, 18.8 ppm;  $\text{C}_{30}\text{H}_{22}\text{O}_8$  (510.49): Calcd C 70.58, H 4.34; Found C 70.64, H 4.33.

## Results and Discussion

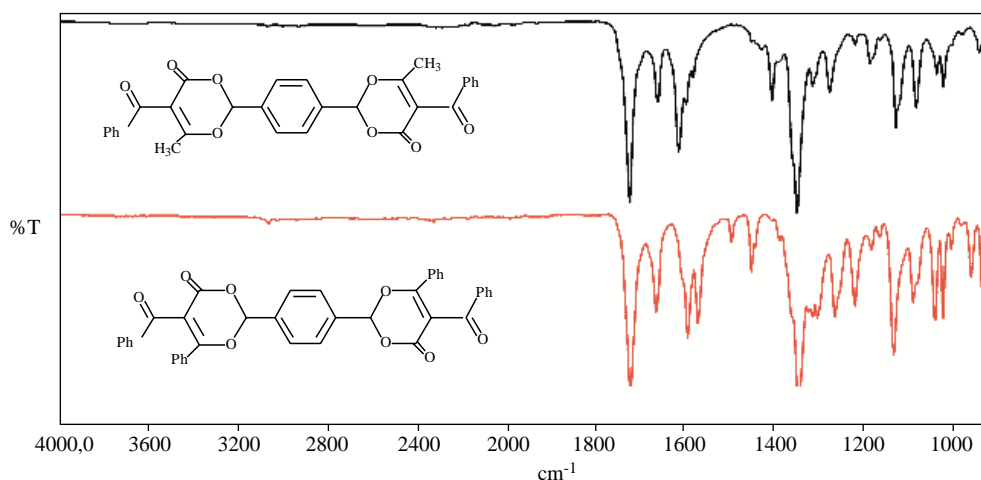
The title compounds **1**, **2**, **3**, and **4** were prepared in moderate yields by the refluxing of equimolar mixtures of corresponding dicarbonyl compounds and oxalyl chloride in the presence of aldehydes in anhydrous xylene or benzene for 1 or 8 h, respectively (Schemes 1 and 2). During this type of reaction, due to the above mentioned reason, side reactions such as dimerization of  $\alpha$ -oxoketenes may occur, which can also explain the moderate yields of the cycloadducts obtained in this work. In the preparation of all these derivatives, both 2,3-furandiones and diacylketenes used for the reactions were generated in situ from equimolar mixtures of diketones and oxalyl chloride in solution containing the corresponding aldehyde. Thus [2+4] cycloaddition of dibenzoylketene generated by decarbonylation of 4-benzoyl-5-phenyl-2,3-furandione<sup>21</sup> formed during one step reaction to C=O moieties of aldehydes led to the formation of some new 1,3-dioxin-4-ones, which provide a practical synthetic method for 5-acyl-1,3-dioxin-4-ones (Scheme 1).



Since both benzoylacetone and acetylbenzoylketene possess unsymmetrical structures, one step reactions between benzoylacetone and oxalylchloride in the presence of aldehydes may produce 2 isomeric 1,3-dioxin-4-one derivatives. However, the results of TLC studies for each reaction illustrate the presence of only one product, the structures of which were identified as 5-benzoyl-6-methyl-2-phenyl-[1,3]dioxin-4-one **3** and 1,4-bis-(5-benzoyl-6-methyl-4-oxo-4*H*-[1,3]dioxin-2-yl)-benzen derivatives **4**. The choice of 1 of the 2 alternative structures is mainly based on the  $^{13}\text{C}$ -NMR spectra of **3** and **4** (it is known that  $^{13}\text{C}$ -NMR signals of C=O moiety of benzoyl groups at C-5 positions of similar compounds appeared approximately at 190-195 ppm while C=O moiety of acetyl groups at the C-5 position of similar compounds gives  $^{13}\text{C}$ -NMR signals approximately at 198-205 ppm)<sup>11,20</sup> (see experimental). This is an indication of regio-specific proceeding of this cycloaddition reaction between acetylbenzoylketene and aldehydes (Scheme 2).



While dibenzoylketene generated in situ from equimolar mixtures of dibenzoylmethane and oxalyl chloride in refluxing solvents showed a pronounced tendency to form [2+4] Diels-Alder adduct when trapped by aldehydes that behave as a heterodienophile in these reactions, the reactions of acetylbenzoylketene generated in situ from equimolar mixtures of benzoylacetone and oxalyl chloride with a part of aldehydes are much more complicated and give dark colored mixtures of substances that are very difficult to separate. This may originate from the presence of an active methyl group in both 4-acetyl-5-phenyl-2,3-furandione<sup>22</sup> and acetylbenzoylketene. The structures of 1,3-dioxinone derivatives obtained in this way were confirmed by analytical and spectral data (see experimental). The <sup>1</sup>H-NMR spectrum exhibits a singlet at  $\delta$  7.10-7.40 ppm for aldehyde adducts.<sup>11-13</sup> In the IR spectra, the presence of C=O absorption bands at approximately 1715-1730  $\text{cm}^{-1}$  besides the absence of -OH vibration bands is characteristic for 1,3-dioxin-4-ones<sup>11</sup> (Figure).



**Figure.** The IR spectra of compounds **2** and **4**.

Consequently, we showed that one step reactions between dibenzoylmethane or benzoylacetone and oxalyl chloride in boiling solvents containing various aldehydes gave some new 1,3-dioxine-4-one derivatives as a practical synthetic method for synthesis of this kind of heterocyclic compound.

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