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Synthesis and properties of aromatic 1,3-diketones and *bis*-(1,3-diketones) obtained from acetophenone and phtalic acids esters

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ABSTRACT

Dibenzoylmethane and six aromatic 1,3-diketones containing a dibenzoylmethane moiety were synthesized from acetophenone and the appropriate ester in crossed-Claisen condensations. The synthesized diketones include derivatives containing carboxyl and ester groups; *bis*-(1,3-diketones) were also prepared. The absorption of UV radiation of the obtained compounds was investigated in various solvents, and their molar absorption coefficients were calculated. The ratio of tautomers and keto-enol equilibrium constants were calculated using ^{1}H NMR techniques. Aromatic *bis*-(1,3-diketones) demonstrated strong hyperchromic effects. The keto-enol equilibrium of the investigated compounds is strongly shifted to the enol form, especially in non-polar solvents.

1. Introduction

Aromatic 1,3-diketones significantly absorb UV-A radiation (λ = 320-400 nm) and are therefore used as sunscreens in cosmetics. Aromatic 1,3-diketones owe this feature to the formation of an intramolecular hydrogen bond in the enol tautomer (Scheme 1). Currently, 1-(4'-tert-butylphenyl)-3-(4''-methoxyphenyl)-propane-1,3-dione is one of the few UV-A sunscreens approved both in Europe and in the USA [1].

The keto-enol equilibrium in 1,3-diketones strongly favors the enol form, and only very polar solvents or steric hindrance cause a slight shift of the equilibrium to the keto form [2]. These compounds also form complexes with metals, a feature which makes these compounds attractive for use in many applications. For example, a complex of a 1,3-diketone with zinc is used as a PVC stabilizer [3] and vulcanization activator [4].

Aromatic 1,3-diketones containing a 1,3-diphenylpropane-1,3-dione (**1**) moiety are synthesized by the condensation of an acetophenone derivative and a substituted ester of benzoic acid (Scheme 2).

Use of phthalic acids esters instead of benzoates leads to aromatic *bis*-(1,3-diketones). Few studies concerning such compounds have been published to date, and these papers mainly describe the chelating properties of *bis*-(1,3-diketones) [5-7]. These compounds form metal complexes, and two chelating centers can form organometallic polymers or triangles [6]. Only two publications have investigated the spectroscopic properties of aromatic *bis*-(1,3-diketones) [8,9]. Because these compounds contain two 1,3-dicarbonyl moieties, they might prove to be superior UV absorbing agents, therefore research of UV absorption properties of *bis*-(1,3-diketones) was the main objective of this work.

2. Experimental

2.1. Instrumentation

The melting points were determined in an open capillary tube on a Stanford Research Systems EZ-Melt MPA120 automated melting point apparatus. NMR spectra were recorded on NMR Varian Inova 300 MHz. UV-VIS spectra were collected on Shimadzu UV-2101 PC double-beam spectrophotometer. Infrared spectra were measured on Mettler-Toledo ReactIR iC10 spectrometer.

2.2. General procedure for synthesis of bis-(1,3-diketones) (1,4)

To a three-necked flask equipped with a mechanical stirrer, reflux condenser and drying tube, 50 mmol of ester, 100 mL of THF and 200 mmol of the base (see Table 1) was added, and the mixture was warmed to the boiling temperature. A mixture of the proper amount of acetophenone (see Table 1) and 25 mL THF was added dropwise over 30 min, and the formation of a yellow solid was observed. The reaction was rapidly stirred for 8 h. The mixture was cooled to 5 °C in an ice bath to avoid ester hydrolysis. Upon cooling, the mixture color changed to dark brown. Neutralization of the formed salt of *bis*-(1,3-diketone) was performed using two methods:

Method 1: Maintaining rapid stirring, 10% HCl was added to the reaction mixture until pH = 7. During neutralization, the mixture color changed to light-yellow. The neutralized mixture was filtered with a Büchner funnel, and the filtrate was poured into a separatory funnel. The aqueous layer was extracted with methylene chloride. Organic fractions were merged and evaporated.

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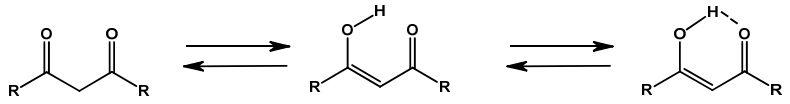
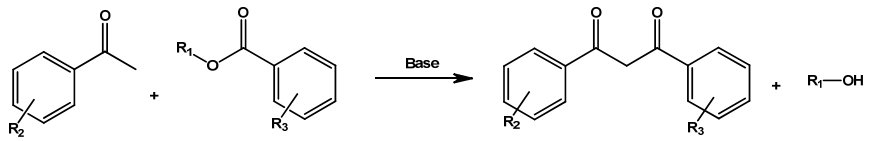


Scheme 1



Scheme 2

From the resulting solid residue, the main products and by-products were separated by column chromatography (100%, CH_2Cl_2). After several crystallizations from methanol, pure *bis*-(1,3-diketones) were obtained. See Table 1 for yields.

Method 2: Maintaining rapid stirring, 100% acetic acid was added to the reaction mixture until pH = 7. During neutralization, the mixture color changed to light-yellow. The gelatinous precipitate containing by-products was centrifuged, and the solution was concentrated and placed in refrigerator for 24 h. The precipitate that formed was filtered and crystallized from DMF/MeOH (1:1; v/v) to give pure product. See Table 1 for yields.

1,4-bis-(3-phenyl-3-oxopropionyl)benzene (**1**): Yellow. M.p.: 177, 197-198 °C (Ref. [8], 176-177 °C). IR (ν_{max}, cm^{-1}): 3060 (w), 2670 (w), 1596 (m), 1529 (s), 1495 (w), 1301 (s-m), 1237 (m), 1184 (m-w), 1159 (w) 1129 (m-w), 1103 (vw), 1069 (m-w), 1028 (w), 1013 (w), 987 (w), 926 (w), 856 (m-w), 800 (m-w), 755 (s), 703 (w), 680 (m). ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 16.82 (2H, br, C(O*H*)=CH-CO), 8.09 (4H, s, Ar-*H*), 8.02 (4H, d, *J*=6.9 Hz, Ar-*H*), 7.59 (2H, t *J*=7.2 Hz, Ar-*H*), 7.52 (4H, t, *J*=7.2 Hz, Ar-*H*), 6.92 (2H, s, C(OH)=C*H*-CO). ^{13}C NMR ($CDCl_3$, 75 MHz, δ, ppm): 187.0, 183.5 (*C*O), 138.7, 135.5, 132.8, 128.8, 127.4, 127.3 (Ar-*C*), 93.7 (C(OH)=*C*H-CO). Anal. Calcd. for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 77.78; H 4.91%.

1,3-bis-(3-phenyl-3-oxopropionyl)benzene (**4**): White. M.p.: 159, 173 °C (Ref. [8] 153-154 °C). IR (ν_{max}, cm^{-1}): 3075 (w), 2672 (w), 1603 (s), 1525 (s), 1484 (s), 1304 (m), 1267 (m), 1241 (m), 1215 (s), 1184 (w), 1159 (w), 1099 (m), 1069 (m), 1024 (m-w), 1002 (m-w), 972 (w), 934 (w), 908 (w), 848 (w), 804 (w), 759 (s), 695 (m), 680 (m), 654 (w). ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 16.89 (2H, br, C(O*H*)=CH-CO), 8.15 (1H, s, Ar-*H*), 8.18 (1H, d, *J*=7.8 Hz, Ar-*H*), 8.02-8.05 (4H, m, Ar-*H*)7.49-7.68(8H, m, Ar-*H*), 6.95 (2H, s, C(OH)=C*H*-CO). ^{13}C NMR ($CDCl_3$, 75 MHz, δ, ppm): 186.4, 185.1 (*C*O), 138.6, 136.5, 133.0, 131.0, 129.4, 129.0, 127.5, 126.0 (Ar-*C*), 93.6 (C(OH)=*C*H-CO). Anal. Calcd. for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 77.75; H, 5.02%.

2.3. General procedure for synthesis of 1,3-diketones with ester group (2,5)

To the three-necked flask equipped with a mechanical stirrer, reflux condenser and drying tube, 50 mmol of ester, 100 mL of THF and 30% solution of sodium methoxide (50 mmol) in methanol was added, and the mixture was warmed to the boiling temperature. The mixture of 33 mmol of acetophenone and 25 mL of THF was added dropwise over 30 min, and the formation of a yellow solid was observed. The reaction was rapidly stirred for 4 h. The mixture was cooled to 5 °C in an ice bath to avoid ester hydrolysis. Upon cooling, the mixture color changed to dark brown. Maintaining rapid stirring, to the reaction mixture 10% HCl was added until pH = 7 was reached. During neutralization, the mixture color changed to light-yellow. The organic layer was separated and evaporated, and the resulting precipitate was filtered and crystallized from methanol to give pure product. Yields: 45% (**2**), 42% (**5**).

Methyl 4-(3-phenyl-3-oxopropionyl)benzoate (**2**): White. M.p.: 123-124 °C (Ref. [10] 123-125 °C). IR (ν_{max}, cm^{-1}): 3057 (w), 2966 (w), 1731 (s), 1596 (s-m), 1529 (s), 1506 (s-m), 1443 (s), 1405 (m-w), 1286 (s), 1230 (m), 1196 (m), 1118 (s), 1073 (m), 1061 (m), 1017 (s), 960 (m-w), 927 (w), 867 (m), 833 (w), 804 (m), 792 (m), 751 (s), 706 (m), 680 (m). ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 16.79 (1H, br, C(O*H*)=CH-CO), 8.15 (2H, d, *J*=8.7 Hz, Ar-*H*), 7.98-8.07(4H, m, Ar-H), 7.59 (1H, t *J*=7.5 Hz, Ar-*H*), 7.51 (2H, t *J*=7.35 Hz, Ar-*H*), 6.90 (1H, s, C(OH)=C*H*-CO) 3.97 (3H, s, -COOC*H3*). ^{13}C NMR ($CDCl_3$, 75 MHz, δ, ppm): 187.1, 183.5 (*C*O), 166.3 (*C*OOCH$_3$), 139.2, 135.4, 133.2, 132.8, 129.8, 128.6, 127.3, 127.0 (Ar-*C*), 93.8 (C(OH)=*C*H-CO), 52.4 (COO*C*H$_3$). Anal. Calcd. for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.30; H, 5.04%.

Methyl 3-(3-phenyl-3-oxopropionyl)benzoate (**5**): White. M.p.: 82-83 °C. IR (ν_{max}, cm^{-1}): 3072 (w), 2956 (w), 2661 (vw), 1727 (s), 1607 (s), 1559 (s), 1480 (s), 1439 (s), 1301 (s), 1263 (s), 1222 (s), 1121 (m), 1076 (m-w), 1065 (w), 1028 (w), 1002 (w), 983 (m-w), 930 (w), 863 (w), 811 (w), 755 (s), 721 (m), 703 (m), 684 (m), 662 (w). ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 16.84 (1H, br, C(O*H*)=CH-CO), 8.63 (1H, s, Ar-*H*), 8.22 (2H, t, J=7.2 Hz, Ar-*H*), 8.02 (2H, d, *J*=6.8 Hz, Ar-*H*), 7.48-7.63 (4H, m, Ar-*H*), 6.92 (1H, s, C(OH)=C*H*-CO), 3.99 (3H, s, -COOC*H3*). ^{13}C NMR ($CDCl_3$, 75 MHz, δ, ppm): 186.5, 184.7 (*C*O), 166.6 (*C*OOCH$_3$), 136.2, 135.5, 133.4, 132.9, 131.7, 131.0, 129.2, 129.0, 128.5, 127.5 (Ar-*C*), 93.5 (C(OH)=*C*H-CO), 52.7 (COO*C*H$_3$). Anal. Calcd. for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.15; H, 5.09%.

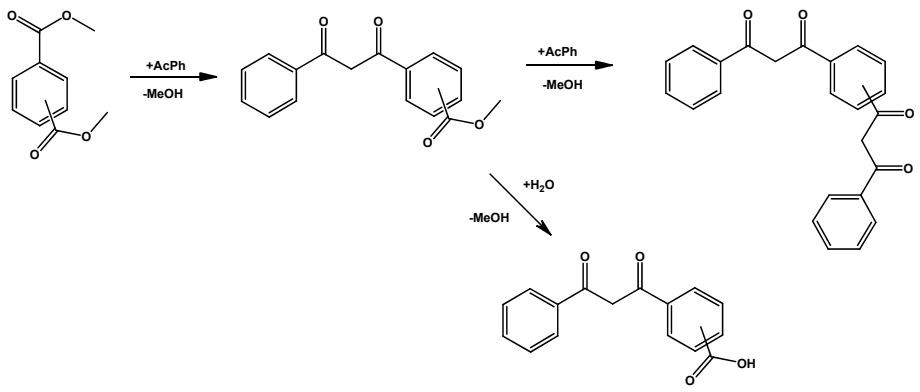
Table 1. Yields and substrates ratio in *bis*-(1,3-diketone) synthesis.

Product	Base	AcPh:Ester [mol:mol]	Yield [%]
1	NaOMe	2.8	50[a]
1	NaH	2.8	61[a]
1	NaOMe	4,0	51[a], 38[b]
1	NaH	4.0	61[a], 49[b]
2	NaOMe	2.8	28[a]
2	NaH	2.8	29[a]
2	NaOMe	4.0	2[a]
2	NaH	4.0	2[a]
4	NaOMe	4.0	44[b]
4	NaH	4.0	64[b]

[a] Determined by HPLC after neutralization with 10% HCl (Method 1).
[b] Separated product after neutralization with 100% CH_3COOH (Method 2).

2.4. General procedure for synthesis of 1,3-diketones with carboxylic group (3,6)

To the round bottom flask proper ester (**2**,**5**) (3,5 mmol), 15 mL of THF and a solution of $LiOH.H_2O$ (35 mmol) in 15 mL H_2O was added. The mixture was stirred with magnetic stirrer for 6h at room temperature. To the separated aqueous layer, 3% HCl (52 mmol) was added.



Scheme 3

The resulting white solid was filtered and crystallized from ethanol to give pure product. Yields: 67% (**3**), 73% (**6**).

4-(3phenyl-3-oxopropionyl)benzoic acid (**3**): White. M.p.: 235 °C. IR (ν_{max}, cm^{-1}): 3027 (m), 2833 (m), 2684 (m), 1682 (s), 1592 (m), 1577 (w), 1532 (m), 1510 (m), 1432 (m), 1327 (w), 1293 (s), 1230 (w), 1189 (w), 1155 (vw), 1121 (m), 1103 (w), 1073 (w), 1058 (w), 1017 (w), 982 (w), 931 (m), 871 (m), 807 (w), 781 (m), 751 (s), 714 (m), 680 (m). ^{1}H NMR (DMSO-d_6, 300 MHz, δ, ppm): 17.04 (1H, br, C(O*H*)=CH-CO), 13.34 (1H, br, -COO*H*), 8.27 (2H, d, *J*=8.4 Hz, Ar-*H*), 8.19 (2H, d, *J*=7.3 Hz, Ar-*H*), 8.08 (2H, d, *J*=8.4 Hz, Ar-*H*), 7.67 (1H, t, *J*=7.4 Hz, Ar-*H*), 7.57 (2H, t, *J*=7.4Hz, Ar-*H*), 7.42 (1H, s, C(OH)=C*H*-CO). ^{13}C NMR (DMSO-d_6, 75 MHz, δ, ppm): 186.7, 183.1 (*C*O), 166.6 (*C*OOH), 138.1, 134.6, 134.2, 133.3, 129.6, 128.9, 127.6, 127.5 (Ar-*C*), 94.1 (C(OH)=*C*H-CO). Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.55; H, 4.64%.

3-(3-phenyl-3-oxopropionyl)benzoic acid (**6**): White. M.p.: 195-196 °C. IR (ν_{max}, cm^{-1}): 2975 (w), 2841 (m), 2672 (w), 1682 (s), 1611 (m), 1532 (m), 1491 (w), 1446 (m) , 1308 (s), 1230 (m), 1185 (w), 1099 (m-w), 1069 (m-w), 1028 (w), 1002 (w), 946 (m), 930 (m), 826 (w), 804 (w), 777 (vw), 748 (s), 706 (m-w), 680 (m), 665 (m). ^{1}H NMR (DMSO-d_6, 300 MHz, δ, ppm): 17.14 (1H, br, C(O*H*)=CH-CO), 13.32 (1H, br, -COO*H*), 8.62 (1H, s, ArH), 8.44 (1H, d, *J*=7.8 Hz, Ar-*H*), 8.15-8.23 (3H, m, Ar-*H*), 7.62-7.74 (2H, m, Ar-*H*), 7.57 (2H, t, *J*=7.4 Hz, Ar-*H*), 7.42 (1H, s, C(OH)=C*H*-CO). ^{13}C NMR (DMSO-d_6, 75 MHz, δ, ppm): 186.6, 184.8 (*C*O), 167.4 (*C*OOH), 135.7, 135.2, 134.1, 133.9, 132.4, 132.3, 130.0, 129.6, 128.5, 128.3 (Ar-*C*), 94.3 (C(OH)=*C*H-CO). Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.58; H, 4.40%.

2.5. Synthesis of 1,3-diphenylpropane-1,3-dione (7)

To a three-necked flask equipped with a mechanical stirrer, reflux condenser and drying tube, 60 mmol of methyl benzoate, 100 mL of THF and 30% solution of sodium methoxide (60 mmol) in methanol was added and mixture was warmed to the boiling temperature. A mixture of 50 mmol of acetophenone and 25 mL of THF was added dropwise over 30 min, and the formation of yellow solid was observed. The reaction was rapidly stirrred for 4 h. The mixture was cooled to 5 °C, and 10% HCl was added until the pH = 7 was reached. The organic layer was separated and evaporated, and the resulting precipitate was filtered and crystallized from ethanol to give pure product. Yield: 80%.

1,3-diphenylpropane-1,3-dione (**7**): White. M.p.: 77-78 °C. IR (ν_{max}, cm^{-1}): 3131 (w), 3069 (m), 2990 (w), 2665 (w), 1600 (s), 1536 (s), 1513 (s), 1488 (s), 1469 (s), 1435 (m), 1308 (s), 1267 (s), 1230 (s), 1185 (m), 1166 (w), 1102 (m), 1065 (m), 1028 (m), 1002 (m), 976 (w), 931 (m), 897 (w), 845 (w), 815 (w), 789 (w-m), 755 (s), 736 (s), 706 (s), 680 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 16.90 (1H, br, C(O*H*)=CH-CO) 7.97-8.01 (4H, m, Ar-*H*), 7.44-7.58 (6H, m, Ar-*H*), 6.86 (1H, s, C(OH)=C*H*-CO). ^{13}C NMR ($CDCl_3$, 75 MHz, δ, ppm): 185.9 (*C*O), 135.7, 132.7, 128.9, 127.4 (Ar-*C*), 93.3 (C(OH)=*C*H-CO). Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.39; H, 5.42%.

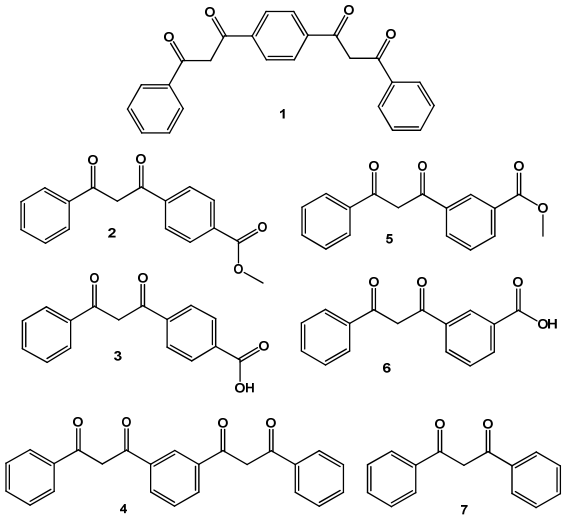
2.6. Melting point

During melting point determination, the transformation in the capillary was observed approximately 20 °C below the typical melting point. The substance was becoming muddy and probably partially melted. The material remained in this state without change until the appropriate melting point temperature was achieved. The existence of two melting points is probably connected with the formation of intramolecular hydrogen bonds and two possible crystalline forms, which may coexist in various ratios depending on which solvent was used for crystallization. Crystallization from DMF/MeOH leads to the formation of large crystals of product containing mainly the form with the higher melting point.

3. Results and discussion

Bis-(1,3-diketones) were obtained by the crossed-Claisen condensation of esters of phthalic acid isomers and acetophenone (Scheme 3) - a modified procedure first reported in [8]. Reactions were conducted in tetrahydrofuran (THF) with a 30% solution of sodium methoxide as a base. Besides *bis*-(1,3-diketones), the intermediate product with one unreacted ester group was found in the reaction mixture (Scheme 3). We investigated the influence of the quantity of acetophenone on *bis*-(1,3-diketone) yield. While an excess of acetophenone decreases the amount of intermediate product, it has little effect on the yield of *bis*-(1,3-diketone). After neutralization of the reaction mixture, we also found 1,3-diketones with carboxylic groups that are formed *via* hydrolysis of the ester group of the intermediate product (Scheme 3).

Thus, we obtained three diketones from dimethyl *p*-phthalate: 1,4-*bis*-(3-phenyl-3-oxopropionyl)benzene (**1**), methyl 4-(3-phenyl-3-oxopropionyl)benzoate (**2**), 4-(3-phenyl-3-oxopropionyl)benzoic acid (**3**), and three diketones from dimethyl *m*-phthalate: 1,3-*bis*-(3-phenyl-3-oxopropionyl) benzene (**4**), methyl 3-(3-phenyl-3-oxopropionyl)benzoate (**5**), 3-(3phenyl-3-oxopropionyl)benzoic acid (**6**). For comparison, we also obtained 1,3-diphenylpropane-1,3-dione (**7**) from methyl benzoate (Scheme 4).



Scheme 4

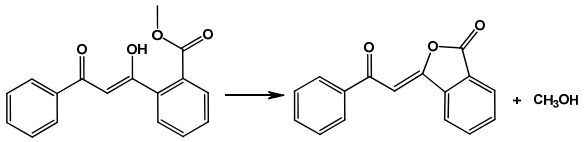
Yields are listed in Table 1. HPLC analysis of the obtained compounds showed that the reaction provides almost complete conversion of the phthalates. The main product after hydrolysis is proper phthalic acid, which is probably formed during hydrolysis with 10% hydrochloric acid. Because of the extremely low solubility of phthalic acids and diketones with carboxylic acid groups (**3**,**6**) and the relatively low solubility of *bis*-diketones (**1**,**4**) (Table 2), these products are difficult to separate. The separation process described in [8], repeated in later publications [5,7], gave contaminated product with low yields.

Table 2. Solubility in g/100 g of solvent of **1**, **2** and **3**.

Product	Solvent	Solubility [g/100 g of solvent]	
		at 21 °C	at boiling temp.
1	Benzene	0.22	-
1	Acetone	-	2.40 (56°C)
1	CH_2Cl_2	1.17	2.27 (39°C)
1	MeOH	0.08	0.10 (65°C)
1	THF	4.42	12.68 (66°C)
1	DMF	4.20	-
1	MeOH/DMF (1/1, v/v)	0.57	4.07 (81°C)
2	CH_2Cl_2	27.87	-
2	MeOH	0.56	5.50 (65°C)
3	Acetone	0.02	-
3	CH_2Cl_2	0.41	-
3	MeOH	0.83	-

Therefore, we carried out several syntheses (method 2), using glacial acetic acid in the hydrolysis step, to prevent formation of diketones with carboxylic acid groups. Using this method, we obtained the by-products as a gelatinous precipitate. After centrifugation and concentration, a relatively pure product precipitated from solution. To achieve high purity, we crystallized the products from a mixture of dimethylformamide and methanol (1:1, v/v), a protocol which required significantly less solvent and increased the crystallization yield relative to that obtained using only methanol as solvent. The use of sodium hydride instead of sodium methoxide increased the yield of *bis*-(1,3-diketones).

When *o*-phthalate was used as the ester in this synthesis, we did not obtain the desired products. However, we isolated a compound that was identified by ^{1}H NMR as mixture of *E* and *Z* isomers of 3-(2'-oxo-2'-phenyl-ethylidene)-*3H*-isobenzofurane-1-one in a ratio of 5:3. This compound probably results from intramolecular transestrification of the intermediate product (Scheme 5).



Scheme 5

3.1. UV absorption

We investigated the UV absorption spectra of the generated compounds in anhydrous ethanol (λ = 210-450 nm), acetonitrile (λ = 210-450 nm) and *n*-heptane (λ = 200-450 nm). The concentration of all solutions was 50±0.5 μmol/dm^3. Because of their low solubility, the spectra of some compounds were not investigated in *n*-heptane. Molar absorption coefficients and absorption maxima are given in Tables 3 and 4. The UV spectra of all obtained compounds in ethanol are given in Figures 1 and 2.

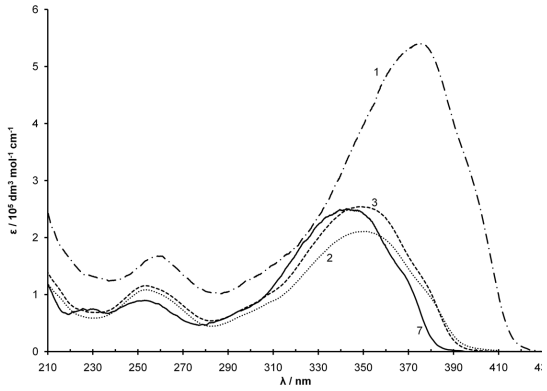


Figure 1. Absorption spectra of **1**, **2**, **3** and **7**. Ethanol, 0.5 cm, 5x10^{-5} mol/dm^3.

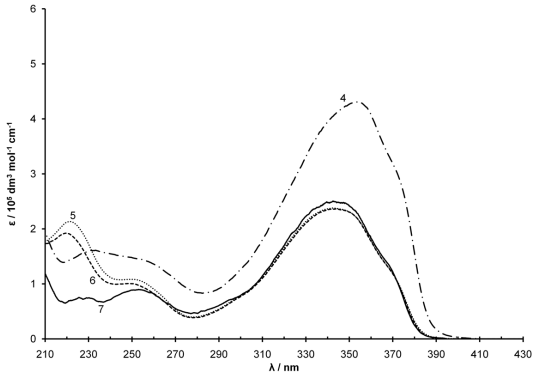


Figure 2. Abosrption spectra of **4**, **5**, **6** and **7**. Ethanol, 0.5 cm, 5x10^{-5} mol/dm^3.

All investigated compounds absorb strongly in the range of λ_1 = 280-400 nm. In addition, two weaker absorption bands can be distinguished: λ_2 = 230-280 nm, λ_3 = 200-230 nm. However, only **7** and compounds synthesized from methyl terephthalate (**1**-**3**) have distinct peaks in band λ_2; peaks of **5** and **6** in this range are barely noticeable, covered by peaks in third band, which come probably from non-conjugated carboxylic group. We found that in the first band, the molar absorption coefficient of **1** is over two times higher than that of **7**, and the absorption maximum is strongly red-shifted. Such strong hyperchromic and bathochromic (Δλ ≈ 33 nm) effects are probably caused by the interaction of two conjugated 1,3-dicarbonyl moieties.

Table 3. Molar absorption coefficients and absorption maxima of synthesized compounds in the range of λ = 280-400 nm.

Product	λ_{max} / nm			ε_{max} / dm³ mol⁻¹ cm⁻¹		
	Ethanol	CH_3CN	*n*-Heptane	Ethanol	CH_3CN	*n*-Heptane
1	375.3	374.5	-	54019	44979	-
2	350.4	347.0	342.7	21066	20373	19748
3	348.7	346.5	-	25409	23636	-
4	354.3	351.6	-	43142	38806	-
5	342.5	341.8	337.5	23789	22622	22686
6	343.1	341.2	-	23636	23333	-
7	342.4	342.0	335.6	25037	23741	23629

Table 4. Molar absorption coefficients and absorption maxima of synthesized compounds in the range of λ = 200-280 nm.

Product	λ_{max} / nm			ε_{max} / dm³ mol⁻¹ cm⁻¹		
	Ethanol	CH_3CN	*n*-Heptane	Ethanol	CH_3CN	*n*-Heptane
1	258.8	256.8	-	16740	14980	-
2	253.2	252.2	252.2	10830	11199	10735
3	253.2	251.8	-	11547	12861	-
4	233.2	233.6	-	16111	16410	-
5	249.7	246.6	247.7	10846	11380	10850
	221.6	219.6	221.0	21333	21460	21352
6	249.0	247.8	-	10067	11619	-
	219.8	219.2	-	19222	21958	-
7	253.0	249.6	248.6	8979	9444	9884

Table 5. Enol percentages and keto-enol tautomerism equilibrium constants of synthesized compounds.

Product	Enol form contents [%]				K_T			
	DMSO-d_6	Acetone-d_6	$CDCl_3$	C_6D_6	DMSO-d_6	Acetone-d_6	$CDCl_3$	C_6D_6
1	95.7	97.9	98.2	>99.9	22	46	53	>999
2	95.4	98.0	>99.9	>99.9	21	49	>999	>999
3	95.1	95.3	98.3	>99.9	20	20	57	>999
4	92.7	97.6	96.8	>99.9	13	41	30	>999
5	92.7	97.0	97.1	>99.9	13	32	33	>999
6	93.1	96.7	97.8	>99.9	13	29	45	>999
7	94.0	97.7	97.8	99.9	16	42	45	999

Table 6. Chemical shifts of characteristic protons of synthesized compounds*.

Product	Chemical shift referenced against TMS / ppm											
	C(O<u>H</u>)=CHCO				C(OH)=C<u>H</u>CO				CO-C<u>H</u>$_2$-CO			
	D	A	C	B	D	A	C	B	D	A	C	B
1	17.11	17.14	16.82	16.33	7.48	7.37	6.92	6.31	4.98	4.91	4.69	-
2	17.01	17.08	16.79	17.21	7.42	7.33	6.90	6.22	4.94	4.89	-	-
3	17.04	17.10	16.74	17.20	7.42	7.35	6.92	6.20	4.94	4.90	4.68	-
4	17.18	17.29	16.89	17.65	7.47	7.41	6.93	6.64	5.02	4.98	4.73	-
5	17.08	17.21	16.85	17.60	7.47	7.35	6.92	6.59	5.02	4.93	4.67	-
6	17.14	17.20	16.83	17.56	7.42	7.35	6.92	6.59	4.95	4.92	4.71	-
7	17.21	17.27	16.90	17.74	7.36	7.27	6.86	6.61	4.89	4.84	4.63	4.10

* D - DMSO-d_6, A - Acetone-d_6, C - $CDCl_3$, B - C_6D_6.

While hyperchromic and bathochromic effects in this band are present with **4**, they are not as strong as those observed with **1**. This finding results from the lack of conjugation between the dicarbonyl groups through the aromatic ring. Intermediate products (**2** and **5**) and by-products (**3** and **6**) do not exhibit the significant spectral effects observed with *bis*-(1,3-diketones), and their spectra are similar to that of **7**. However, we observed small bathochromic effects for **2** (Δλ ≈ 8 nm) and **3** (Δλ ≈ 6 nm), which arise from the conjugation of the 1,3-dicarbonyl group with ester or carboxylic acid groups.

3.2. Keto-enol tautomerism

We determined the enol percentage of each diketone by recording their ^{1}H NMR spectra at ambient temperature in four solvents: DMSO-d_6, acetone-d_6, $CDCl_3$ and benzene-d_6. The keto-enol equilibrium constant was calculated using the formula: K_T = [enol] / [keto].

The concentration of all solutions was 100±10 mmol/dm^3. Enol percentages and keto-enol tautomerism constants are given in the Table 5. Chemical shifts of the characteristic protons are given in Table 6. Influence of solvent is slight; however, the equilibrium is increasingly shifted to the keto form as solvent polarity is increased. In deuterated benzene, the equilibrium is shifted to the enol form to such an extent that a peak corresponding to the characteristic protons of the keto form was not observed (except **7**).

4. Conclusion

We investigated the UV-absorption and keto-enol tautomerism of seven 1,3-dicarbonyl compounds. The keto-enol equilibrium constant of all compounds suggests that the equilibrium favors the enol form. With increasing solvent polarity, the equilibrium slightly shifts to the keto form, a finding which probably results from the association of polar solvent with the keto tautomers. Keto tautomers are more polar than the pseudo-cyclic, intramolecularly-bonded enol tautomers. Domination of the enol tautomer results in strong absorption of radiation in the UV-A range by all investigated compounds, regardless of the solvent used. The absorption profile of the aromatic 1,3-diketones with carboxylic acid and ester groups is similar to that of 1,3-diphenylpropane-1,3-dione (**7**). However, aromatic *bis*-(1,3-diketones) show strong bathochromic and hyperchromic effects which result from the presence of two 1,3-dicarbonyl moieties. The strongest

hyperchromic effect is observed for **1**, where the dicarbonyl groups are conjugated through the aromatic ring. This conjugation also causes the strong bathochromic shift and absorption in visible range of the radiation. This effect on the absorption profile of **1** gives rise to its yellow color, which obviates some of its applications. In the case of **4**, we observed a somewhat smaller, but still very strong hyperchromic effect, with significantly smaller bathochromic effects resulting from the non-conjugated dicarbonyl groups. Because of its better absorption properties in comparison to other 1,3-diketones, compound **4** has a chance to become a promising future substitute for currently used sun-protective agents.

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