

# Photochemical behaviour of $\alpha$ -diketones on a silica gel surface: a novel photoreaction by intramolecular trapping of an excited ketone carbonyl oxygen by an aryl group

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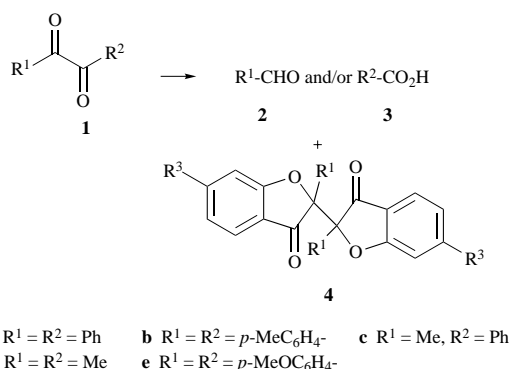
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Irradiation of the benzils **1a,b** having the lowest  $n,\pi^*$  excited state on dry silica gel with a high-pressure mercury lamp gives the benzoic acids **3a,b** and bibenzofuranones **4a,b**, whereas irradiation of 1-phenylpropane-1,2-dione **1c** and biacetyl **1d** gives acetaldehyde and/or benzoic acid; under these conditions, 4,4'-dimethoxybenzil **1e**, the lowest excited state of which is possibly the  $\pi,\pi^*$  state, fails to react.

The photochemistry of carbonyl compounds has been thoroughly investigated and their behaviour is well established. Such compounds undergo Norrish Type I reactions,<sup>1</sup> Type II reactions,<sup>2</sup> pinacol formation through intermolecular hydrogen abstraction,<sup>2</sup> or Paterno–Buchi reactions.<sup>3</sup> Although these photoreactions usually occur in solution, some of them also proceed on solid supports such as silica gel or alumina.<sup>4–8</sup> Photoreactions on non-reactive solid supports have received much attention, since such a surface can provide an ordered two-dimensional environment for effecting and controlling photochemical processes.<sup>4b,9,10</sup> Such photoreactions observed on the surface are fundamentally the same as those seen in solution, although large differences in the product distributions have been observed in some cases.<sup>4,6,7</sup> We recently reported that some ketones show different photochemical behaviour on a silica gel surface from that in solution; 2-benzoylcyclohexanone underwent a Type I as well as a Type II photoreaction on a silica gel surface<sup>5</sup> while giving an exclusive Type II reaction in solution.<sup>11</sup> Organic molecules may undergo distortion of their conformation by adsorption on the surface, and the distortion may give a new photoreactivity to the molecules. We report here on the novel surface photoreaction of diaryl  $\alpha$ -diketones through unprecedented intramolecular trapping of an excited ketone carbonyl oxygen by an aryl group, and on possible uses of the surface as a reaction field for inducing new types of photoreactions.

## Results and discussion

Irradiation of benzil **1a** on dry silica gel with a 100 W high-pressure mercury lamp gave benzoic acid **3a** (59%) and the bibenzofuranone **4a** (16%). The IR spectrum of compound **4a** showed a peak due to the lactone carbonyl at  $1720\text{ cm}^{-1}$ , and the <sup>1</sup>H NMR spectrum showed only peaks attributable to aromatic protons at  $\delta$  7.0–7.6. The parent peak at  $m/z$  418 in the mass spectrum and the elemental analysis indicate a molecular formula of  $\text{C}_{28}\text{H}_{18}\text{O}_4$ . These data support the structure **4a**. Compound **4a** should exist as a mixture of ( $\pm$ )- and *meso*-isomers. Indeed, the <sup>13</sup>C NMR spectrum showed the presence of two isomers, the ratio of which is nearly 1:1, although the isomers could not be isolated. Irradiation of **1b** under the same conditions also gave **3b** (41%) and **4b** (23%). On the other hand, irradiation of **1c** and **1d** under the same conditions gave only the  $\alpha$ -cleavage products **2c** (60%), **3c** (60%) and **2d** (30%). In these cases no bibenzofuranones were detected. The bibenzo-



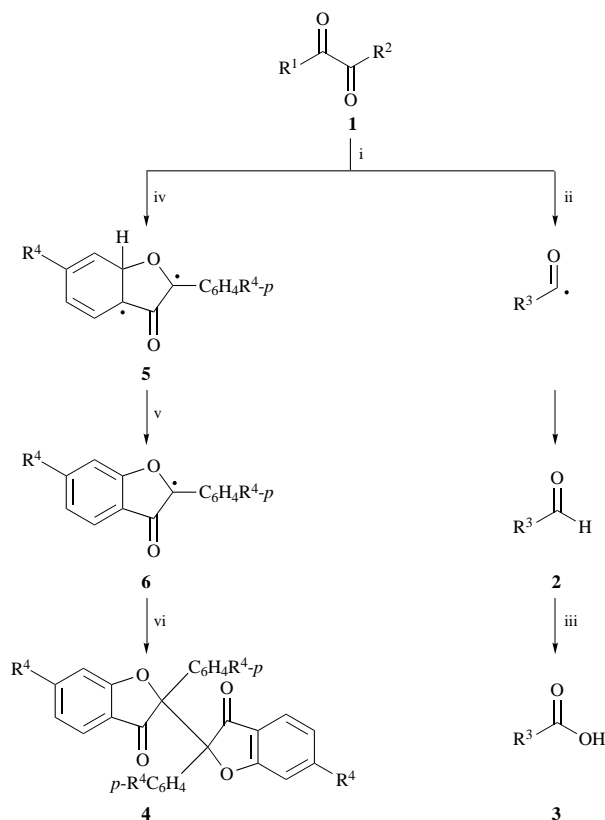
**Scheme 1** Conditions:  $h\nu$  on  $\text{SiO}_2$

furanones **4a,b** are products characteristic of the surface photoreaction of diaryl  $\alpha$ -diketones **1a,b**. The bibenzofuranone **4a** could not be detected in solution photochemistry of benzil **1a**. Thus, it is noteworthy that the silica gel surface provides a new reaction field for inducing novel photoreactions.

Formation of **2c,d** and **3a–c** can be explained in terms of  $\alpha$ -cleavage, as in the surface photoreaction of 2-benzoylcyclohexanone. Irradiation of benzaldehyde on a dry silica gel surface, gave benzoic acid as the sole photoproduct. Therefore, the failures of **1a–c** to give aryl aldehydes can be reasonably explained in terms of the surface photoreaction of such initially formed compounds to afford the corresponding carboxylic acids. Because it does not absorb light above 300 nm, acetaldehyde failed to give acetic acid.

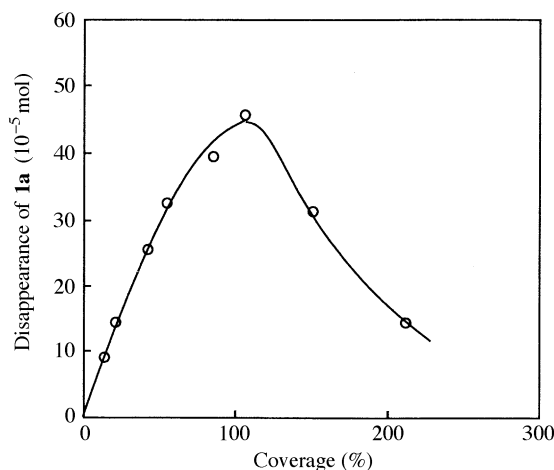
Formation of the bibenzofuranones can be explained in terms of coupling of the radical intermediate **6** produced from the biradical intermediate **5** which is probably formed by the intramolecular radical trapping of excited carbonyl oxygen by an aryl ring. Transformation from the biradical **5** to the radical **6** is an aromatization step, so that the loss of hydrogen occurs easily. Since no benzofuranone<sup>12</sup> was detected and the bibenzofuranones were produced under degassed conditions, the hydrogen may be trapped by the silica gel surface. Consequently oxygen molecules on the surface may react with the hydrogen because perfect degassing of the adsorbed oxygen may not have been achieved by the usual freeze–pump–thaw cycle.

The trapping of excited carbonyl oxygen by an aryl ring occurred only in diaryl  $\alpha$ -diketones **1a,b**. This indicates that stabilization of the radical centre in the intermediate **5** by an aryl group is required for the trapping reaction. Irradiation of



**Scheme 2** Conditions and reagents: i,  $h\nu$  on  $\text{SiO}_2$ ; ii,  $\text{R}^3 = \text{R}^1$  or  $\text{R}^2$ , iii, (O),  $\text{R}^3 = \text{Ph}$  or  $p\text{-MeC}_6\text{H}_4$ ; iv,  $\text{R}^4 = \text{H}$  or  $\text{Me}$ ; v,  $-\text{H}\cdot$ ; vi, dimerization

**1e**, the lowest excited state of which is possibly  $\pi, \pi^*$ , gave no photoproducts. Therefore, the formation of the aldehydes **2**, the acids **3** and bibenzofuranones **4** occurs from the lowest  $n, \pi^*$  excited state of the  $\alpha$ -diketones. The trapping should require overlap of the singly occupied n-orbital located on the carbonyl oxygen and the  $p\pi$ -orbital on an *ortho*-carbon of a benzene ring. These orbitals are perpendicular to each other when the molecular skeleton is planar. However, the long-wavelength band of benzil in the UV absorption spectrum is not at 450 nm as in glyoxal but at 370 nm, and the spectrum resembles that of benzaldehyde. The two aryl groups are twisted with respect to each other by as much as  $90^\circ$  if each carbonyl group in the  $\alpha$ -diketones is strongly conjugated and co-planar with the aryl group to which it is attached.<sup>13</sup> In the ground state of benzil, both in the crystal and in solution, the two benzoyl groups are approximately planar and the groups join together with a torsion angle of  $108^\circ$ , although the molecule is free to twist about its central carbonyl-carbonyl bond.<sup>14</sup> Benzaldehyde and benzil give the characteristic emission spectra of mono- and  $\alpha$ -dicarbonyl molecules, with triplet-state energies of 71.9 and 54.3 kcal mol<sup>-1</sup>, respectively.<sup>15</sup> Hence strong interaction between the two benzoyl units is inferred in the excited benzil molecule. In the most excited state configuration of benzil possible, the phenyl groups are perpendicular to the planar dicarbonyl system.<sup>16</sup> The distance between the carbonyl oxygen and *ortho*-carbon in the excited state configuration of benzil is longer than in the co-planar structure, so that the singly occupied n-orbital and the  $p\pi$ -orbital on the *ortho*-carbon cannot overlap. This is probably the reason why the trapping does not occur following photochemical irradiation of the diaryl  $\alpha$ -diketones in solution. The overlap of these orbitals can be brought about by some distortion of the molecular conformation in the excited state. Formation of **4a**, **4b** from **1a**, **1b** on the silica gel surface through the intermediate **5** indicates that diaryl  $\alpha$ -diketone molecules adsorbed on the surface would have a conformation sufficiently distorted to cause the overlap of these orbitals; that is, the distortion of conformation on the surface causes the new photoreactivity of the molecules.



**Fig. 1** Dependence of the coverage on the extent of disappearance of the starting material in the surface photoreaction of **1a**. A 1 g amount of silica gel was used for all runs. The coverage was determined from calculations using space-filling models.

**Table 1** Yields of photoproducts **2**, **3** and **4**

$\alpha$ -Diketone <b>1</b>	Yield (%) <sup>a</sup>		
	<b>2</b>	<b>3</b>	<b>4</b>
a	Trace	59	16 <sup>b</sup>
b	Trace	41	23 <sup>c</sup>
c	60 <sup>d</sup>	60	0
d	30 <sup>d</sup>	0	—
e	0	0	0

<sup>a</sup> Based on the amount of consumed starting material. <sup>b</sup>  $\text{R}^3 = \text{H}$ . <sup>c</sup>  $\text{R}^3 = \text{Me}$ . <sup>d</sup> Isolated as 2,4-dinitrophenylhydrazone.

The coverage on the surface by the molecules must be an important factor for surface photoreactions because the character of the reaction environment changes at 100% coverage. The monolayer coverage can be determined from the Langmuir adsorption isotherm<sup>4a,4c,17</sup> or by calculations based on the surface area of silica gel and the area occupied by one molecule determined from space-filling models.<sup>4a,4c,5,18</sup> The values of the monolayer coverage obtained from these two methods generally show good agreement.<sup>4a,4c</sup> Thus, the monolayer coverage was determined from the calculation using the space-filling model. The surface area per gram of the silica gel used (Merck Kieselgel 60, Art. 7734) was 494 m<sup>2</sup>. The area per molecule of **1a** was estimated to be  $ca. 1.12 \times 10^{-18}$  m<sup>2</sup> by using space-filling models, whence 100% coverage is estimated as  $ca. 7.3 \times 10^{-4}$  mol g<sup>-1</sup>. When the ratio of **1a** to silica gel is over  $7.3 \times 10^{-4}$  mol g<sup>-1</sup>, multiple layers must be formed. The effect of surface coverage on the photoreaction of **1a** was studied using sample loadings of different amounts of **1a** on 1 g of the silica gel. Fig. 1 shows the relationship between the amounts of **1a** loaded on the silica gel and the amounts of **1a** which disappeared under the same irradiation conditions. The amounts of **1a** which disappeared increased initially with an increase in the amounts loaded, reaching a maximum at near 100% coverage, and then decreased. No bibenzofuranones were detected at coverages exceeding 200%. These results strongly indicate that the adsorption on the surface causes a new photoreactivity of **1a**.

In conclusion, diaryl  $\alpha$ -diketones underwent a novel photoreaction to form bibenzofuranones on a silica gel surface through the radical intermediate produced from trapping of the singly occupied n-orbital located on the carbonyl oxygen by the  $p\pi$ -orbital on an *ortho*-carbon in the benzene ring. The distortion of molecular conformation suitable for this novel trapping reaction probably occurred by initial adsorption on the silica gel surface.

## Experimental

Mps are uncorrected. IR spectra were recorded with a JASCO IR Report-100 instrument.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured with a JEOL JNM-LA400 or Bruker AM400 spectrometer using  $\text{CDCl}_3$  as a solvent and tetramethylsilane as an internal standard. Mass spectra were measured with a JEOL JMS-AX 505W mass spectrometer. GLC analysis was performed using a Shimadzu GC-8A gas chromatograph equipped with a flame-ionization detector using a 2 m column containing 3% SE 30. A Taika 100 W high-pressure mercury lamp was used as an irradiation source. The starting  $\alpha$ -diketones **1a–e** were commercially available material and were used without further purification. Silica gel (Merck Kieselgel 60, Art. 7734) was used as received.

### General procedure for irradiation of **1** on dry silica gel

The  $\alpha$ -diketone **1** (ca. 2.0 mmol) in dichloromethane (5  $\text{cm}^3$ ) was added to silica gel (5 g) in a 100  $\text{cm}^3$  round-bottomed flask. The mixture was sonicated for 5 min after which the solvent was evaporated under reduced pressure. The coated silica gel, divided into six nearly equal portions, was then placed in Pyrex tubes (18  $\times$  180 mm). In the experiments under oxygen-free conditions the tubes were degassed by three freeze–pump–thaw cycles and sealed. The tubes were rotated and irradiated for 48 h with a 100 W high-pressure mercury lamp. The irradiated silica gel was collected. Acetone (20  $\text{cm}^3$ ) was added to the silica gel to extract the organic components and the mixture was sonicated for 10 min. The silica gel was filtered off and washed with acetone (10  $\text{cm}^3$ ). The combined filtrate and washings were then evaporated under reduced pressure. More than 93% of organic material based on the weight of the starting diketone used was recovered by this method. The residue was chromatographed on silica gel. Elution with a mixture of acetone–hexane (1:6, v/v) gave unchanged diketone and photoproducts. The structure of the photoproducts **2** and **3** were determined by direct comparison with commercial samples.

**2,2'-Diphenyl-2,2'-bibenzofuran-3-(2H)-one 4a.** Obtained as a ( $\pm$ )-*meso* mixture (isomer **A**:**B** = 52:48); mp 176–178 °C (from dichloromethane–hexane) (Found: C, 80.4; H, 4.4.  $\text{C}_{28}\text{H}_{18}\text{O}_4$  requires C, 80.4; H, 4.3%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1720 (C=O);  $\delta_{\text{H}}(400 \text{ MHz})$  7.0–7.6 (18 H, m, ArH);  $\delta_{\text{C}}(400 \text{ MHz})$  isomer **A**: 90.5 (s, 2 C), 113.1 (d, 2 C), 121.6 (s, 2 C), 122.2 (d, 2 C), 124.5 (d, 4 C), 127.1 (d, 4 C), 127.9 (d, 2 C), 128.9 (d, 2 C), 131.0 (s, 2 C), 137.8 (d, 2 C), 170.1 (s, 2 C) and 196.4 (s, 2 C); isomer **B**: 89.9 (s, 2 C), 112.8 (d, 2 C), 121.2 (s, 2 C), 122.2 (d, 2 C), 124.7 (d, 4 C), 127.3 (d, 4 C), 127.9 (d, 2 C), 128.9 (d, 2 C), 131.2 (s, 2 C), 137.9 (d, 2 C), 170.8 (s, 2 C) and 196.2 (s, 2 C);  $m/z$  418( $\text{M}^+$ ) and 209.

**2,2'-Di-*p*-tolyl-2,2'-bibenzofuran-3-(2H)-one 4b.** Obtained as a ( $\pm$ )-*meso* mixture (**A**:**B** = 49:51); mp 269–271 °C (from dichloromethane–hexane) (Found: C, 81.0; H, 5.6.  $\text{C}_{32}\text{H}_{26}\text{O}_4$  requires C, 81.0; H, 5.5%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1710 (C=O);  $m/z$  474 ( $\text{M}^+$ ) and 237; isomer **A**  $\delta_{\text{H}}(400 \text{ MHz})$  2.30 (6 H, s, 2  $\times$  Me), 2.37 (6 H, s, 2  $\times$  Me) and 6.8–7.5 (14 H, m, ArH);  $\delta_{\text{C}}(400 \text{ MHz})$  22.5 (q, 4 C), 91.2 (s, 2 C), 113.2 (d, 2 C), 119.4 (s, 2 C), 123.6 (d, 2 C), 124.2 (d, 2 C), 127.9 (d, 4 C), 128.0 (d, 4 C), 128.6 (s, 2 C),

138.5 (s, 2 C), 149.7 (s, 2 C), 171.2 (s, 2 C) and 195.7 (s, 2 C); isomer **B**  $\delta_{\text{H}}(400 \text{ MHz})$  2.31 (6 H, s, 2  $\times$  Me), 2.36 (6 H, s, 2  $\times$  Me) and 6.8–7.5 (14 H, m, ArH);  $\delta_{\text{C}}(400 \text{ MHz})$  21.2 (q, 4 C), 90.2 (s, 2 C), 112.9 (d, 2 C), 118.9 (s, 2 C), 123.6 (d, 2 C), 124.3 (d, 2 C), 127.8 (d, 4 C), 127.9 (d, 4 C), 128.5 (s, 2 C), 138.6 (s, 2 C), 149.8 (s, 2 C), 171.6 (s, 2 C) and 196.2 (s, 2 C).

### Photolysis of **1a** on a silica gel surface at different coverages

An appropriate amount of **1a** was dissolved in dichloromethane (5  $\text{cm}^3$ ) and the solution was added to silica gel (1 g) in a Pyrex tube (18  $\times$  180 mm). The mixture was sonicated for 5 min after which it was evaporated under reduced pressure. The tubes were rotated and irradiated for 48 h with a 100 W high-pressure mercury lamp. To the adsorbed material was added acetone (5  $\text{cm}^3$ ) containing a known amount of eicosane (ca. 0.1 mmol) as a calibrant for the GLC analysis and the mixture was sonicated for 10 min. The supernatant fluids were analysed by gas chromatography.

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