

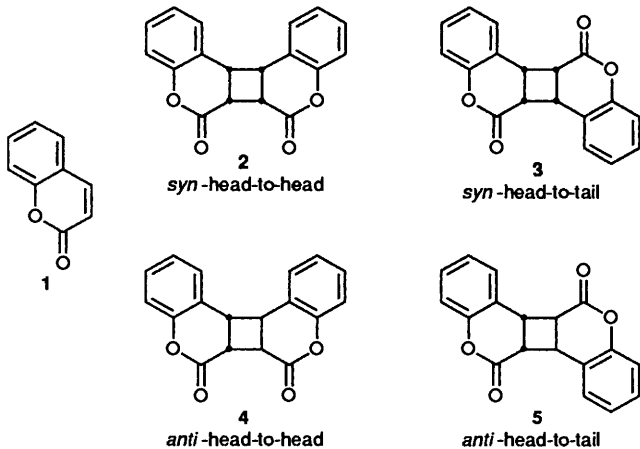
## Selective Photodimerisations of Coumarin in Crystalline Inclusion Compounds

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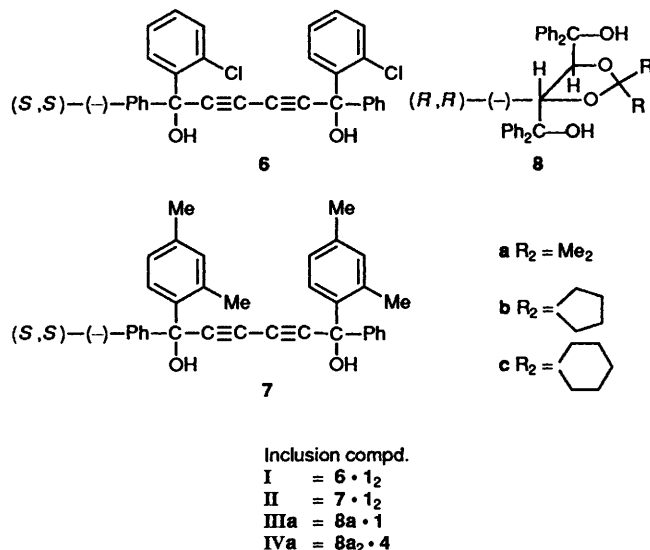
Selective photodimerisations of coumarin **1** as the guest in inclusion compounds are reported. For example, irradiation of two 1:1 crystalline inclusions of **1** with (*R,R*)-(-)-*trans*-4,5-bis-(hydroxydiphenylmethyl)-2,2-dimethyl-1,3-dioxacyclopentane **8a** prepared by recrystallisation of the component from toluene-hexane and ethyl acetate-hexane gave *syn*-head-to-head **2** and (-)-*anti*-head-to-head dimer **4** with 96% e.e.

Photoreactions of coumarin **1** in EtOH both in the absence and in the presence of benzophenone as a sensitizer give, respectively, a mixture of *syn*-head-to-head dimer **2** (m.p. 279–280 °C) and *syn*-head-to-tail dimer **3** (m.p. 204–206 °C),<sup>1</sup> and *anti*-head-to-head dimer **4** (m.p. 181–182 °C) together with a small amount of *anti*-head-to-tail dimer **5** (m.p. 320–325 °C).<sup>2</sup> Dimerisation in CH<sub>2</sub>Cl<sub>2</sub> gives a complex mixture of which the major product is **2**.<sup>3</sup> Photoreaction of crystalline **1** carried out in the expectation of a stereoselective dimerisation, failed to give any product.<sup>4–6</sup> Our success with stereoselective photoreactions of guest compounds included in an appropriate host<sup>7,8</sup> prompted us to investigate the selective photodimerisation of **1**. We found that photoirradiation of a 1:2 inclusion crystal **I** of (*R,R*)-(-)-1,6-di(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol **6**<sup>9</sup> and of a 1:2 inclusion crystal **II** of (*R,R*)-(-)-1,6-(2,4-dimethylphenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol **7**<sup>10</sup> with **1** in the solid state gives **2** and **5**, respectively.



Interestingly, however, irradiation of a 1:1 inclusion crystal **IIIa** of (*R,R*)-(-)-*trans*-4,5-bis-(hydroxydiphenylmethyl)-2,2-dimethyl-1,3-dioxacyclopentane **8a**<sup>11</sup> with **1** prepared by recrystallisation of the two components from ethyl acetate-hexane gave (-)-**4** of 96% e.e., although the same irradiation of a 1:1 inclusion crystal of **8a** and **1** prepared by recrystallisation from toluene-hexane gave **2**. We also found that the photoreaction proceeds very efficiently upon irradiation of a stirred aqueous suspension of powdered inclusion crystal.

A suspension of powdered **I** (m.p. 134–135 °C) (5.0 g) in water



(100 cm<sup>3</sup>) containing a small amount of sodium alkyl sulfate as a surfactant was irradiated † for 5 h. The reaction mixture was filtered, washed with water, dried, and washed with hot MeOH to leave crude **2**. Recrystallisation of the crude product from CHCl<sub>3</sub> gave pure **2** as colourless prisms (1.4 g, 74.5%, m.p. 279–281 °C). However, irradiation of powdered **I** itself for 22.5 h gave **2** in only 17.5% yield. Photoconversion of **1** into **2** by the irradiation of powdered **I** in the solid state has also been carried out recently by the Venkatesan research group.<sup>12</sup>

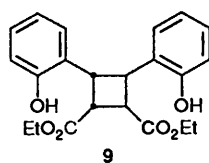
Irradiation of a suspension of powdered **II** (m.p. 97–101 °C) (1.0 g) in water (100 cm<sup>3</sup>) containing the surfactant for 4 h gave *rac*-**5** as colourless prisms (0.35 g, 92.1%, m.p. 320–325). The photoreaction proceeded very slowly when powdered **II** was irradiated in the solid state. For example, irradiation of powdered **II** with 400 W high-pressure Hg-lamp for 20.5 h gave *rac*-**5** in 94% yield.

Recrystallisation of **8a** (10.0 g, 21.5 mmol) and **1** (3.2 g, 21.9 mmol) from AcOEt (20 cm<sup>3</sup>)-hexane (100 cm<sup>3</sup>) gave the 1:1 inclusion crystal **IIIa** as colourless needles (5.7 g, 43%, m.p. 95–98 °C). Irradiation of powdered **IIIa** (1 g) in water (100 cm<sup>3</sup>) containing surfactant for 3 h gave a 2:1 complex **IVa** of **8a** and (-)-**4** of 96% e.e. as colourless needles (0.96 g, 96%, m.p. 228–232 °C). This complex was too stable to allow replacement of the guest by another molecule. Heating of **IVa** (0.96 g) with conc. HCl in EtOH under reflux for 30 min gave the ester (-)-**9** (96% e.e.) as colourless prisms {0.22 g, 75%, m.p. 174–175 °C, [α]<sub>D</sub> -104 ‡ (c 0.18, MeOH)}. The optical purity of (-)-**9** was determined by HPLC on the chiral solid phase, Chiralcel OJ. § Heating of (-)-**9** in AcOH under reflux for 24 h gave (-)-**4** of (96% e.e. quantitatively {m.p. 168–169 °C, [α]<sub>D</sub> -8.6 (c 0.11,

† All irradiations were carried out at room temperature by using 100 W high-pressure Hg-lamp, unless otherwise stated.

‡ [α]<sub>D</sub> Values quoted in units of 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup>.

§ Chiralcel OJ is available from Daicel Chemical Industries, Ltd., Himeji, Japan.



benzene)}. When powdered **IIIa** was irradiated directly, it took 9 h to complete the reaction.

Recrystallisation of **IIIa**, m.p. 95–98 °C initially prepared, from toluene–hexane (1 : 5) gave **IIIa** m.p. 90–92 °C as colourless prisms. Irradiation of a suspension of powdered **IIIa**, m.p. 90–92 °C (3.0 g) in water (100 cm<sup>3</sup>) containing the surfactant for 30 h gave **2** (0.31 g, 43.1%). The photoreaction in the solid state was very inefficient; for example, no significant change occurred when **IIIa**, m.p. 90–92 °C was irradiated for 10 h.

Not only is the difference in the photochemical reaction of the two 1 : 1 inclusion complexes between **8a** and **1** interesting, but also the ready interconversion between the two complexes upon recrystallisation. This probably arises as a result of differences in molecular arrangement of **1** in the two complexes. This agent is to be studied by X-ray crystal structure analysis.

It is also unclear as to why only *rac*-**5** is obtained in the photoreaction of **II**, an enantioselective photoreaction of the guest usually occurring in the inclusion crystal with an optically active host.<sup>7,8</sup> Nevertheless, the optically active host compounds, **6**, **7** and **8a**, seem to be important for the efficient and selective photodimerisation of **1**, the achiral host compound 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol<sup>13</sup> failing in this respect. Thus, irradiation of the inclusion complex of the latter and **1** (1 : 2) in the solid state and as an aqueous suspension failed to give any photodimer. The 1 : 1 inclusion compounds of **1** with (*R,R*)-(-)-*trans*-2,3-bis(hydroxydiphenylmethyl)-1,4-dioxaspiro[4.4]nonane **8b**<sup>8</sup> and with (*R,R*)-(-)-*trans*-2,3-bis-

(hydroxydiphenylmethyl)-1,4-dioxaspiro[5.4]decane **8c**<sup>11</sup> were similarly inert.

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