Regio- and Enantio-selective Photodimerisation of Cyclohex-2-enone as an Inclusion Complex with a New Optically Active Host, (−)-1,4-Bis[3-(*o*-chlorophenyl)-3-hydroxy-3-phenylprop-1-ynyl]benzene: Preparation of the Optically Pure (−)-*syn-trans*-Dimer of Cyclohex-2-enone

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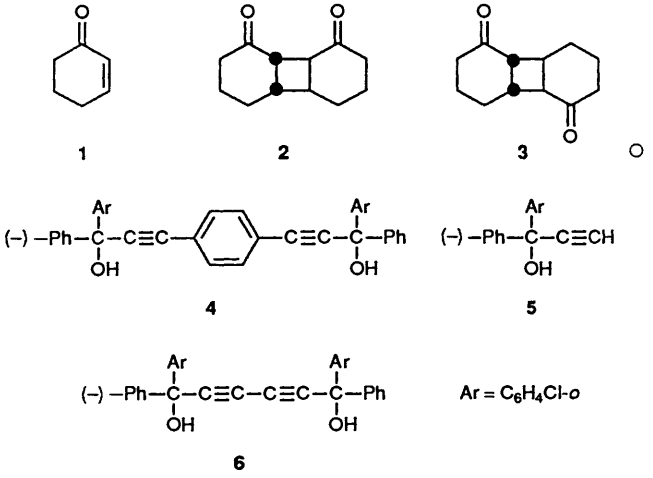
Photoirradiation of a 1:2 inclusion compound of (−)-1,4-bis[3-(*o*-chlorophenyl)-3-hydroxy-3-phenylprop-1-ynyl]benzene and cyclohex-2-enone as an aqueous suspension gave the (−)-*syn-trans*-dimer of cyclohex-2-enone in 48% ee, which on an optical resolution by complexation with (−)-1,6-bis(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol afforded the optically pure enantiomer.

Photoirradiation of both neat and benzene solutions of cyclohex-2-enone **1** give a complex mixture of the *syn-trans*-**2** and *anti-trans*-dimer **3**,† and two other dimers of unknown structure.[1] Here, we report regio- and enantio-selective photodimerisation of **1** as an inclusion complex with a new (see later) chiral host, (−)-1,4-bis[3-(*o*-chlorophenyl)-3-hydroxy-3-phenylprop-1-ynyl]benzene **4** to give (−)-**2** in 48% ee selectively in 74.8% yield. Complexation of the dimer **2** (48% ee) with (−)-1,6-bis(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol **6**,[2] afforded optically pure (−)-**2**. Photodimerisation of **1** proceeds more efficiently when the powdered inclusion complex of **1** and **4** is irradiated as an aqueous suspension rather than when it is irradiated directly.



A solution of **4** (5.0 g, 8.94 mmol) and **1** (1.72 g, 17.9 mmol) in ether–hexane (1:1, 10 cm^3) was kept at room temperature for 6 h to give a 1:2 complex of **4** and **1** as colourless prisms (6.1 g, 91%), m.p. 90–95 °C. A suspension of the powdered complex (4.2 g) in a water (100 cm^3) containing a small amount of sodium alkylsulfate as surfactant was irradiated‡ at room temperature for 24 h. The reaction mixture was filtered, dried, and distilled *in vacuo* to give (−)-**2** in 48.0% ee as an oil (0.8 g, 74.8%), $[\alpha]_D$ −61.0§ (*c* 0.4, MeOH).

In contrast, irradiation of the solid powdered complex of **4** and **1** for 24 h, gave compound **2** in 46.5% ee (41.5% yield). It is unclear why the photoreaction of the aqueous suspension is the more efficient process. The identity of **2** was established by comparison of its gas chromotographic retention time with that of an authentic sample prepared by a literature method.[1] The optical purity of **2** was determined by comparison of its $[\alpha]_D$ value with that of an optically pure sample prepared as follows.

A solution of **6** (1.51 g, 3.13 mmol) and **2** (48.0% ee) (0.6 g, 3.13 mmol) in toluene (10 cm^3) was kept at room temperature for 12 h to give a 1:1 complex of **6** and **2**. The complex was thrice recrystallised from toluene to give crystals of the pure complex; the latter when distilled *in vacuo* afforded optically pure **2** (0.27 g, 61.4%), $[\alpha]_D$ −127 (*c* 0.56, MeOH). The optical purity of **2** was established on the basis that by further complexation with **6** its $[\alpha]_D$ value was unchanged.

The mechanism of the regio- and enantio-selective photodimerisation of **1** in the inclusion complex with **4** will, it is hoped, be clarified by a future X-ray analysis of the complex.

For the selective photodimerisation of **1**, the new host **4** was the most effective whilst compound **6** was ineffective. The new host **4** was prepared by coupling an acetylenic compound and a halogenoarene.[3] Optically pure **5**[4] (53.5 g, 220 mmol), *p*-dibromobenzene (26.0 g, 110 mmol), $PdCl_2(PPh_3)_2$ (0.1 g), CuI (0.1 g), PPh_3 (0.52 g) and Et_3N (280 ml) were mixed and heated under reflux for 4 h. After remains of Et_3N·HBr by filtration, the Et_3N solution was evaporated to leave crude **4**. Recrystallisation of this from acetone gave a 1:2 complex of pure **4** and acetone as colourless prisms, m.p. 81–82 °C, which when heated *in vacuo* gave optically pure **4** as white powder [49.3 g, 80.2%, $[\alpha]_D$ −62.6 (*c* 1.13, MeOH)], m.p. 82–83 °C.

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† The structure was elucidated by X-ray crystal structure analysis. The data will be published in the near future.
‡ Photoirradiations were carried out using a 100 W Hg lamp.
§ $[\alpha]_D$ Values are given in 10^{-1} deg cm^2 g^{-1} throughout.

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