

Stereoselective Photocycloadditions of Chalcone Derivatives in a Crystalline Inclusion Complex with 1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol

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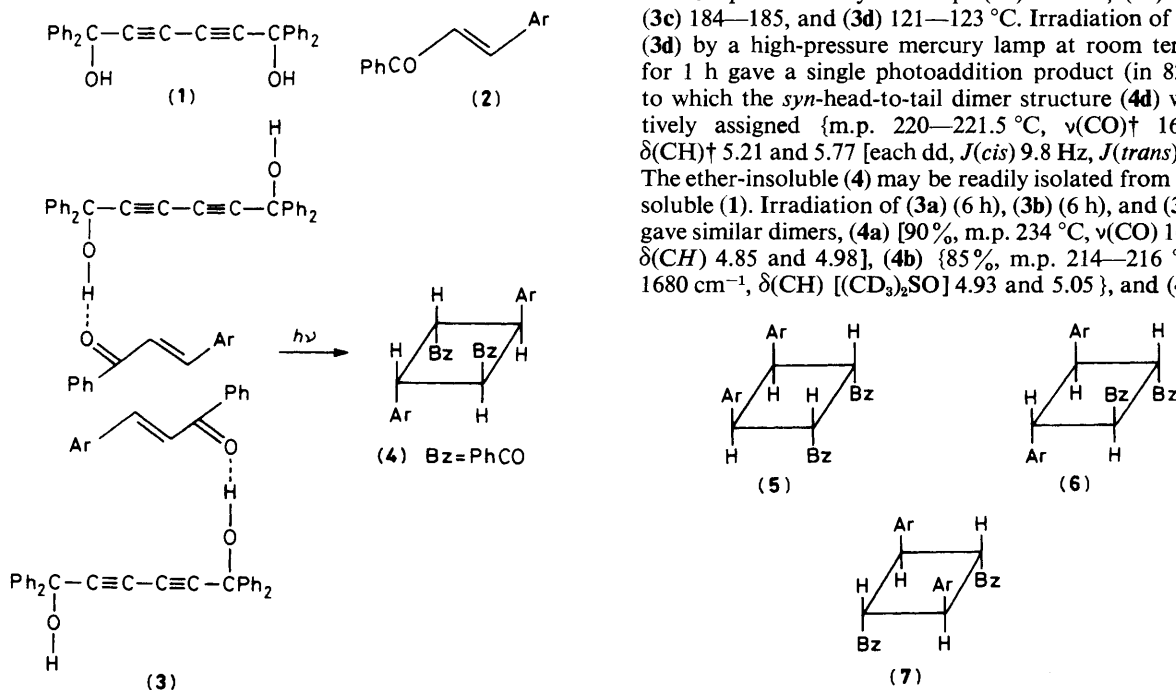
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Irradiation of complexes of chalcone derivatives with 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol, in the crystalline state, gave only the *syn*-head-to-tail cycloaddition product.

1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol (1) includes various guest molecules in a definite ratio and forms crystalline host-guest complexes.¹ An X-ray structural study of the 2:1 acetone complex of (1) shows that the acetone is included in a channel formed by the host molecule (1) and that the hydrogen bond between host and guest molecules is important.² When

guest molecules are arranged close together in the channel, intermolecular reactions may proceed stereoselectively and efficiently. We now report an example of such a reaction.

When diethyl ether solutions of (1) and 2 mol. equiv. of (2a—d) were allowed to stand for 3 h at room temperature, complexes (3a—d) were formed as colourless prisms in almost quantitative yield: m.p. (3a) 87—89, (3b) 110—112, (3c) 184—185, and (3d) 121—123 °C. Irradiation of powdered (3d) by a high-pressure mercury lamp at room temperature for 1 h gave a single photoaddition product (in 82% yield) to which the *syn*-head-to-tail dimer structure (4d) was tentatively assigned {m.p. 220—221.5 °C, $\nu(\text{CO})\dagger$ 1660 cm^{-1} , $\delta(\text{CH})\dagger$ 5.21 and 5.77 [each dd, $J(\text{cis})$ 9.8 Hz, $J(\text{trans})$ 6.6 Hz]}. The ether-insoluble (4) may be readily isolated from the ether-soluble (1). Irradiation of (3a) (6 h), (3b) (6 h), and (3c) (1.5 h) gave similar dimers, (4a) [90%, m.p. 234 °C, $\nu(\text{CO})$ 1680 cm^{-1} , $\delta(\text{CH})$ 4.85 and 4.98], (4b) [85%, m.p. 214—216 °C, $\nu(\text{CO})$ 1680 cm^{-1} , $\delta(\text{CH})$ [(CD₃)₂SO] 4.93 and 5.05}, and (4c) [88%,



a; Ar = Ph
 b; Ar = *o*-MeC₆H₄
 c; Ar = *o*-MeOC₆H₄
 d; Ar = 1-naphthyl
 e; Ar = *o*-ClC₆H₄
 f; Ar = 2-furyl
 g; Ar = 2-thienyl

† All the i.r. spectra were measured in Nujol mull. All the n.m.r. spectra were measured at 100 MHz in CDCl₃, unless otherwise noted.

m.p. 171–173 °C, $\nu(\text{CO})$ 1675 cm^{-1} , $\delta(\text{CH})$ 4.97 and 5.10], respectively. Although the n.m.r. spectra of (4a), (4b), and (4c) could not be analysed directly, these dimers seem to have similar structures to that of (4d).

There are three other possible structures for the photodimer of *trans*-chalcone, *syn*-head-to-head (5), *anti*-head-to-head (6), and *anti*-head-to-tail (7). Structures (5) and (6) would show two doublet methine proton signals and (7) would show two triplet methine proton signals in the n.m.r. spectrum. Structure (4) was assigned tentatively from the two double-doublet methine proton signals of (4d), that were actually observed.† There is little possibility that the photodimer is derived from the corresponding *cis*-chalcone: since irradiation of (3a) for 0.5 h gave (4a) (24%) and (2a) (73%) but none of the *cis*-chalcone, *cis*-*trans* isomerisation of (2a) is not concerned in the photodimerisation. Also, *cis*-chalcones do not form host-guest complexes with (1).

Irradiation of (2a) in solution gives a mixture of (2a) and its *cis*-isomer³ or a polymer.⁴ Irradiation of (2a) in the solid state gives a complex mixture of stereoisomeric photodimers in low yield,⁴ although photodimerisation of alkenes in the

solid state has been successful in some cases.⁵ The high stereoselectivity and the efficiency of the photodimerisation in (3) suggests that pairs of molecules of (2) are arranged at the best distance apart in the channel for *syn* and head-to-tail dimerisation.

Interestingly, we found that complexes with relatively weak hydrogen bonds between host and guest molecules are inert to the photodimerisation. In contrast with the reactive, tightly hydrogen-bonded (3a) [$\nu(\text{OH})$ 3300 cm^{-1}], (3b) (3310 cm^{-1}), (3c) (3300 cm^{-1}), and (3d) (3300 cm^{-1}), complexes (3e) [m.p. 133–135 °C, $\nu(\text{OH})$ 3330 cm^{-1}], (3f) [m.p. 101–102 °C, $\nu(\text{OH})$ 3380 cm^{-1}], and (3g) [m.p. 80–81 °C, $\nu(\text{OH})$ 3400 cm^{-1}] were inert to the irradiation.

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† As requested by a referee, 400 MHz n.m.r. spectra of (4a) [$\delta(\text{CH})$ 4.85 and 4.95] and (4d) [$\delta(\text{CH})$ 5.21 and 5.77 [each dd, $J(\text{cis})$ 10.0 Hz, $J(\text{trans})$ 7.2 Hz]] were also measured. However, the spectrum of (4a) could still not be analysed directly.