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

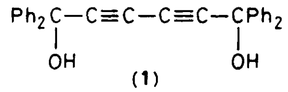
Koichi Tanaka and Fumio Toda*

Department of Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790, Japan

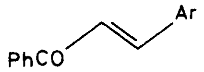
Irradiation of complexes of chalcone derivatives with 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol, in the crystalline state, gave only the *syn*-head-to-tail cycloaddition product.

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.

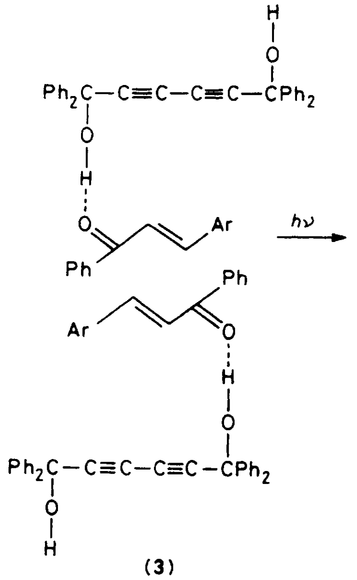
When diethyl ether solutions of (**1**) and 2 mol. equiv. of (**2a**—**d**) were allowed to stand for 3 h at room temperature, complexes (**3a**—**d**) were formed as colourless prisms in almost quantitative yield: m.p. (**3a**) 87—89, (**3b**) 110—112, (**3c**) 184—185, and (**3d**) 121—123 °C. Irradiation 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, ν(CO)† 1660 cm^{-1}, δ(CH)† 5.21 and 5.77 [each dd, *J*(*cis*) 9.8 Hz, *J*(*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, ν(CO) 1680 cm^{-1}, δ(C*H*) 4.85 and 4.98], (**4b**) {85%, m.p. 214—216 °C, ν(CO) 1680 cm^{-1}, δ(CH) [$(CD_3)_2SO$] 4.93 and 5.05}, and (**4c**) [88%,



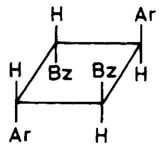
(**1**)



(**2**)

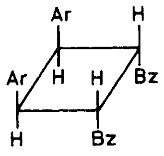


(**3**)

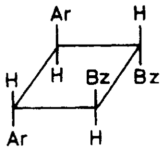


(**4**) Bz = PhCO

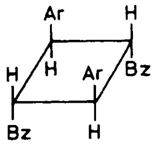
a; Ar = Ph
b; Ar = *o*-MeC_6H_4
c; Ar = *o*-$MeOC_6H_4$
d; Ar = 1-naphthyl
e; Ar = *o*-ClC_6H_4
f; Ar = 2-furyl
g; Ar = 2-thienyl



(**5**)



(**6**)



(**7**)

---

† All the i.r. spectra were measured in Nujol mull. All the n.m.r. spectra were measured at 100 MHz in $CDCl_3$, unless otherwise noted.

m.p. 171—173 °C, ν(CO) 1675 cm^{-1}, δ(C*H*) 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*-chalones do not form host–guest complexes with (**1**).

Irradiation of (**2a**) in solution gives a mixture of (**2a**) and its *cis*-isomer[3] 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**) [ν(OH) 3300 cm^{-1}], (**3b**) (3310 cm^{-1}), (**3c**) (3300 cm^{-1}), and (**3d**) (3300 cm^{-1}), complexes (**3e**) [m.p. 133—135 °C, ν(OH) 3330 cm^{-1}], (**3f**) [m.p. 101—102 °C, ν(OH) 3380 cm^{-1}], and (**3g**) [m.p. 80—81 °C, ν(OH) 3400 cm^{-1}] were inert to the irradiation.

Received, 4th January 1983; Com. 014

---

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

References

1 F. Toda and K. Akagi, *Tetrahedron Lett.*, 1968, 3695.

2 F. Toda, D. L. Ward, and H. Hart, *Tetrahedron Lett.*, 1981, **22**, 3865.

3 R. E. Lutz and R. H. Jordan, *J. Am. Chem. Soc.*, 1950, **72**, 4090.

4 H. Stobbe and K. Bremer, *J. Prakt. Chem.*, 1929, **123**, 1.

5 L. Addadi, J. van Mil, and M. Lahav, *J. Am. Chem. Soc.*, 1982, **104**, 3422; J. van Mil, L. Addadi, E. Gati, and M. Lahav, *ibid.*, p. 3429.