

# Enantioselective Photoreactions of Tropolone Alkyl Ethers in a Crystalline Inclusion Complex with Optically Active 1,6-Di(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol

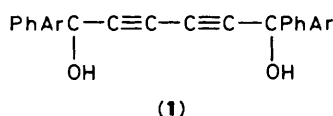
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Irradiation of complexes of tropolone alkyl ethers with optically active 1,6-di(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol in the crystalline state gave the [2 + 2] photoreaction product, 1-alkoxybicyclo[3.2.0]hepta-3,6-dien-2-one, and its ring-opened derivative, alkyl 4-oxocyclopent-2-ene-1-acetate, in 100 and 72–91% enantiomeric excess.

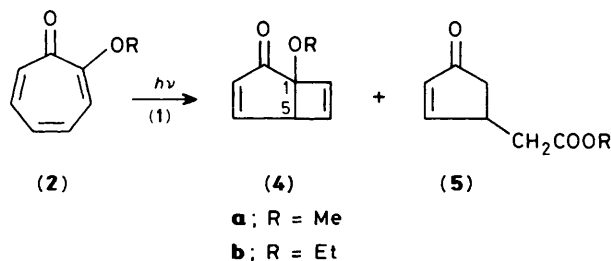
Stereoselective photoreactions of guest compounds included into 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol (**1a**) have been reported.<sup>1–3</sup> Enantioselective photoreaction is expected when an optically active host compound is used instead of (**1a**). We now report the title reaction as an example of such reaction.

When a solution of (*R*)-(-)-(**1b**)<sup>4,5</sup> and an equimolar amount of (**2a,b**) in benzene-*n*-hexane (1:1) was allowed to stand for 12 h at room temperature, 1:1 complexes (**3a,b**) were formed as colourless needles in almost quantitative yields: (**3a**) m.p. 69–71°C,  $[\alpha]_D -92.2^\circ$ ; (**3b**) m.p. 135–137°C,  $[\alpha]_D -104^\circ$ .<sup>†</sup> Irradiation of powdered (**3a**) by a high-pressure mercury lamp at room temperature for 72 h (50% conversion) gave (1*S*,5*R*)-(-)-1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (**4a**) {11% yield,  $[\alpha]_D -168^\circ$ , 100% enantiomeric excess (e.e.)} and (*S*)-(+)-methyl 4-oxocyclopent-2-ene-1-acetate (**5a**) (26% yield,  $[\alpha]_D +89.5^\circ$ , 91% e.e.). Similar irradiation of (**3b**) for 83 h (50% conversion) gave (1*S*,5*R*)-(-)-(**4b**) (12% yield,  $[\alpha]_D -189^\circ$ , 100% e.e.) and (*S*)-(+)-(**5b**) (14% yield,  $[\alpha]_D +59.3^\circ$ , 72% e.e.). Separation of (**4**) and (**5**) was carried out by column chromatography on silica gel using CHCl<sub>3</sub> as a solvent. The optical purity of (**4**) and (**5**) was determined by h.p.l.c. using a column containing an optically active solid phase, Chiralcel.<sup>‡</sup> The optical purity of (**5a**) was also confirmed by comparing its  $[\alpha]_D$  with the reported value.<sup>6</sup> The absolute configurations of (**4**) and (**5**) have been studied.<sup>6</sup>



**a**; Ar = Ph

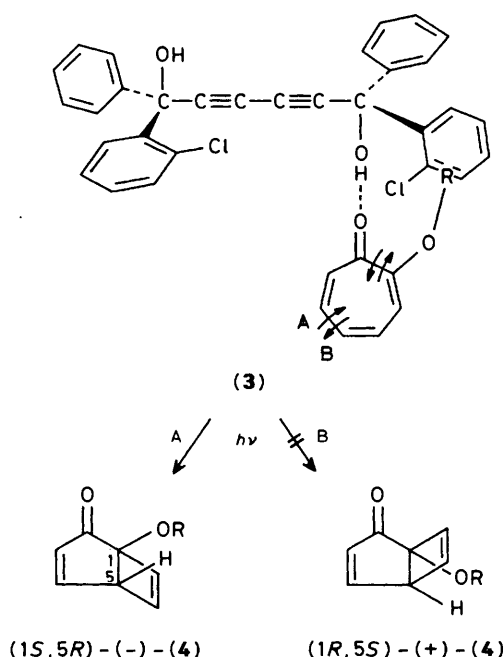
**b**; Ar = *o*-ClC<sub>6</sub>H<sub>4</sub>



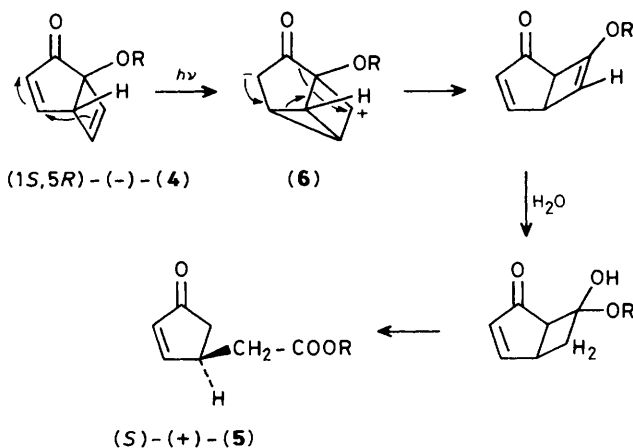
<sup>†</sup> All the  $[\alpha]_D$  values were measured in MeOH at a concentration (*c*) of 0.2.

<sup>‡</sup> Chiralcel is available from Daicel Chemical Industries, Ltd., Himeji, Japan.

The enantioselective photoreaction of (**2**) to (**4**) in the complex with (**1b**) can be interpreted as follows: in a 1:1 complex of (*R*)-(-)-(**1b**) and (**2**), disrotatory [2 + 2] photoreaction of (**2**) occurs only in the A direction but not B direction according to a steric hindrance of the *o*-chlorophenyl group (Scheme 1), and gives (1*S*,5*R*)-(-)-(**4**) but not (1*R*,5*S*)-(+)-(**4**).



**Scheme 1.** A possible view of the enantioselective photoreaction of (**2**) in the crystalline inclusion complex with (*R*)-(-)-(**1b**).



**Scheme 2**

Formation of **(5a)** (91% e.e.) and **(5b)** (72% e.e.) in the photoreaction of **(3a)** and **(3b)**, respectively, shows that the conversion of **(4)** into **(5)** (Scheme 2)<sup>7</sup> proceeds with relatively low enantioselectivity. This is probably due to a small amount of water contaminant in the complex; the irradiation of **(4a)** (100% e.e.) and **(4b)** (100% e.e.) in 2% aqueous MeOH gave **(5a)** (45% e.e.) and **(5b)** (35% e.e.), respectively. It was also disclosed that this low enantioselective conversion of **(4)** into **(5)** is due to a photochemical racemisation of **(5)** via its reversible enolisation. Irradiation of a 2% aqueous MeOH solution of **(5a)** (97% e.e.) and **(5b)** (72% e.e.) for 4 h gave **(5a)** (34% e.e.) and **(5b)** (27% e.e.), respectively. However, the racemisation occurred very slowly in a dry MeOH solution. Contrarily, these results would support that the photochemical course from **(4)** to **(5)** does not contain any racemisation step. However, the enantioselectivity of the conversion of **(4)** into **(5)** in a crystalline inclusion complex could not be confirmed, since **(4)** did not form a complex with **(1b)**.

We thank Professor Toyonobu Asao of Tohoku University for a kind gift of tropolone.

Received, 6th June 1986; Com. 767

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