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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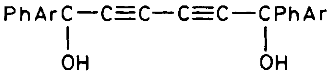
Irradiation of complexes of tropolone alkyl ethers with optically active 1,6-di(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol in the crystalline state gave the [2 + 2] photoreaction product, 1-alkoxybicyclo[3.2.0]hepta-3,6-dien-2-one, and its ring-opened derivative, alkyl 4-oxocyclopent-2-ene-1-acetate, 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.[1—3] 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**)[4,5] 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°; (**3b**) m.p. 135—137 °C, $[\alpha]_D$ −104°.† 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°, 100% enantiomeric excess (e.e.)} and (*S*)-(+)-methyl 4-oxocyclopent-2-ene-1-acetate (**5a**) (26% yield, $[\alpha]_D$ +89.5°, 91% e.e.). Similar irradiation of (**3b**) for 83 h (50% conversion) gave (1*S*,5*R*)-(−)-(**4b**) (12% yield, $[\alpha]_D$ −189°, 100% e.e.) and (*S*)-(+)-(**5b**) (14% yield, $[\alpha]_D$ +59.3°, 72% e.e.). Separation of (**4**) and (**5**) was carried out by column chromatography on silica gel using $CHCl_3$ 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.‡ The optical purity of (**5a**) was also confirmed by comparing its $[\alpha]_D$ with the reported value.[6] The absolute configurations of (**4**) and (**5**) have been studied.[6]

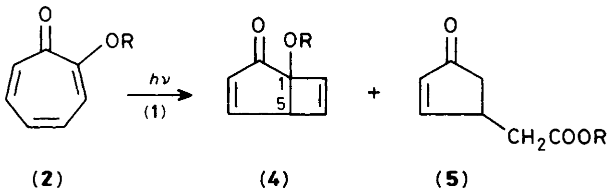


$$\underset{\mathrm{OH}}{\underset{|}{\mathrm{PhArC}}}-\mathrm{C}\equiv\mathrm{C}-\mathrm{C}\equiv\mathrm{C}-\underset{\mathrm{OH}}{\underset{|}{\mathrm{CPhAr}}}$$

(**1**)

a; Ar = Ph

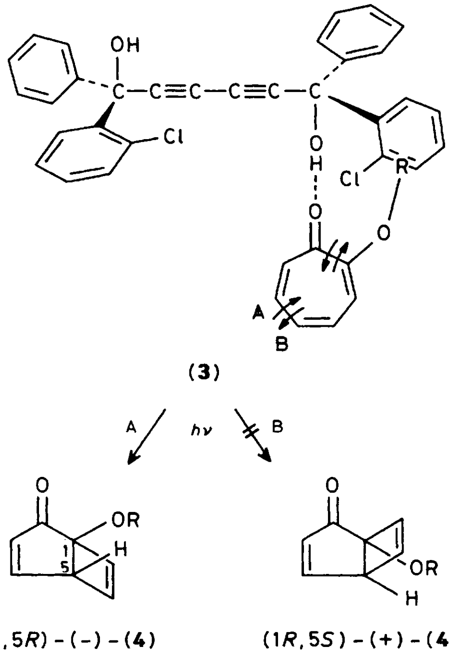
b; Ar = *o*-ClC_6H_4



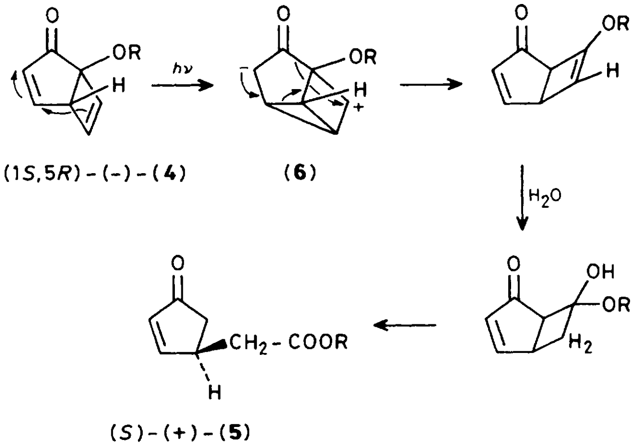
a; R = Me

b; R = Et

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

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

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

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)[7] 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**).

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