Control of the Stereochemistry in the Photocyclisation of Acrylanilides to 3,4-Dihydroquinolin-2(1*H*)-ones. Delicate Dependence on the Host Compound

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The stereochemistry of the photocyclisation of acrylanilides to 3,4-dihydroquinolin-2(1*H*)-ones is controlled almost completely by irradiation in a crystalline inclusion compound with an optically active host compound derived from tartaric acid; the configuration of the photocyclisation product is controlled delicately by two hosts with slightly different structures.

The photocyclisation of acrylanilide to 3,4-dihydroquinolin-2(*H*)-one was first reported in 1971,[1] and its application to alkaloid synthesis has long been studied.[2] In this reaction, stereocontrol, especially, enantiocontrol is important. However, no attempt of enantiocontrol in this reaction has been reported except for one enantioselective photocyclisation of acrylanilide **6** in benzene–diethyl ether containing (+)-di(*p*-toluoyl)tartaric acid which affords 3,4-dihydroquinolin-2-one **7** in 12–16% enantiomeric excess (e.e.).[3]

We report almost perfect control of the photocyclisation of anilides **2**, **6**, **8** and **10** to the corresponding, almost optically pure, 3,4-dihydroquinolin-2-ones, **4, 7, 9** and **11**, respectively.

Inclusion crystals of the anilides and the host **1** were prepared by the following method: for example, when a solution of **1a**[4] (2.5 g, 5.08 mmol) and **2** (0.96 g, 5.08 mmol) in diethyl ether (20 ml)–hexane (5 ml) was kept at room temperature for 2 days, 1:1 inclusion crystals of **1a** and **2** were obtained as colourless crystals (2.92 g, 84% yield, m.p. 95–98 °C). By a similar method, a 1:1 complex of **1b**[5] and **2** was prepared. All other 1:1 complexes of **6, 8** and **10** with **1a** and **1b** prepared by a similar method and the melting points are summarized in Table 1.

Irradiation† of finely powdered 1:1 complex of **1a** with **2** (1.0 g) for 150 h gave, after purification of the crude reaction mixture by chromatography on silica gel using benzene–THF (15:1) as solvent, (−)-**4** of 98% e.e. {0.122 g, 46% yield, m.p. 98–100 °C, $[\alpha]_D$ −68.0 (*c* 0.05, MeOH)}.[6] On the other hand, the same irradiation of a 1:1 complex of **1b** with **2** gave (+)-**4** of 95% e.e. in 29% yield.‡ The striking enantiocontrol of the enantioisomeric hosts **1a** and **1b** to afford the (−)- and (+)-products, respectively, was also found in the photocyclisation of **6, 8** and **10** (Table 1). In the case of **10**, however, the optical yield of (+)-**11** was very low.

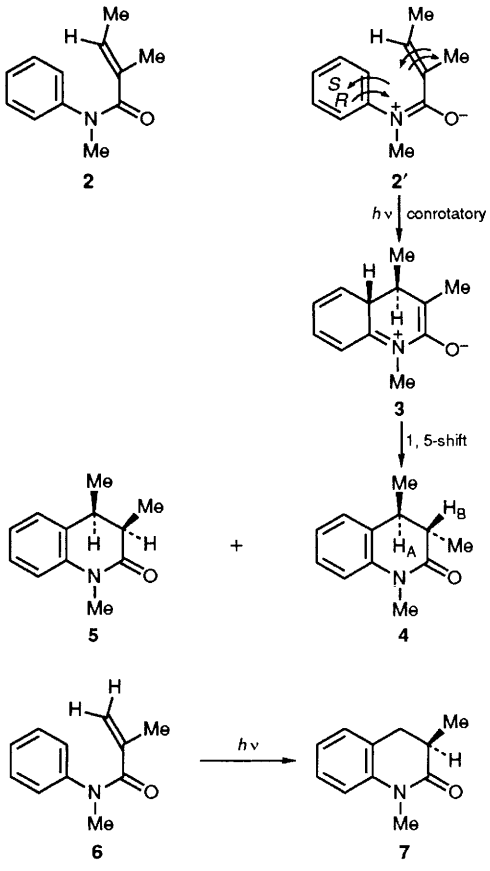
Table 1 Photocyclisation of anilides **2, 6, 8** and **10** in 1:1 inclusion complexes with the hosts **1a** and **1b**

				Product		
Anilide	Host	M.p. of complex/°C	Reaction time/h	Yield (%)[d]		Optical purity (% e.e.)
2	**1a**	95–98	150	(−)-**4**	46	98
2	**1b**	—[a]	150	(+)-**4**	29	95
6	**1a**	99–102	150	(−)-**7**	65	98
6	**1b**	—[a]	150[b]	(+)-**7**	44	98
8	**1a**	118–121	50[c]	(+)-**9**	62	70
8	**1b**	121–124	50[c]	(−)-**9**	29	99
10	**1a**	123–124	15[c]	(−)-**11**	64	98
10	**1b**	102	15[c]	(+)-**11**	41	8

[a] Did not show clear melting point. [b] When the irradiation was carried out in a suspension of water containing sodium alkylsulfate as a surfactant the reaction ceased within 50 h. [c] Reactions were carried out in a suspension in water containing sodium alkylsulfate as a surfactant. [d] Isolated yield in the pure state.

† Photoirradiations were carried out at room temperature using a 400 W high-pressure Hg-lamp. All $[\alpha]_D$ values were measured in MeOH. All optical purities of the products were determined by HPLC on an optically active solid phase, Chiralcel OC (Daicel Chemical Industries, Ltd., Himeji, Japan).

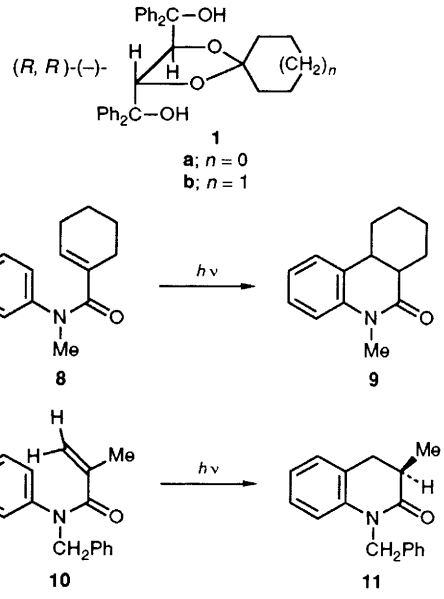
‡ The *trans*-structure in **4** was elucidated by comparison of its J_{HAHB} value (4.0 Hz) with that of *cis*-isomer **5** (4.8 Hz).



Scheme 1

Although the photocyclisation of the complex in the solid state took a long time, the photoreaction of powdered complex in a suspension in water containing sodium alkylsulfate as a surfactant proceeded efficiently (Table 1).

The selective photocyclisation of **2** to **4** in the inclusion crystal with **1** can be interpreted as follows: of the two possible directions (*S* and *R*) in the conrotatory ring closure of the enol form (**2′**) of **2**, only the rotation towards the *S* direction, for example, occurs by control with the host **1a** (or **1b**) to give the intermediate **3**. Which direction the conrotatory ring closure of **2′** occurs within which inclusion complex (**1a** or **1b**) will be determined by X-ray crystal structure analysis. The 1,5-hydrogen shift on **3** which probably proceeds in a suprafacial manner is also controlled precisely by the host **1** and finally gives *trans*-isomer **4**. When the irradiation of **2** was carried out in solution, a 1 : 1 mixture of racemic **4** and **5** was obtained. The enantioselective photocyclisation of **6, 8** and **10** can also be interpreted in similar manner (Scheme 1). The stereochemistry of **9** was found to be *trans*.[6]



During our study of selective reactions in inclusion crystals,[7] we have not encountered such a delicate control of the reaction by hosts of slightly different structures such as **1a** and **1b**.

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