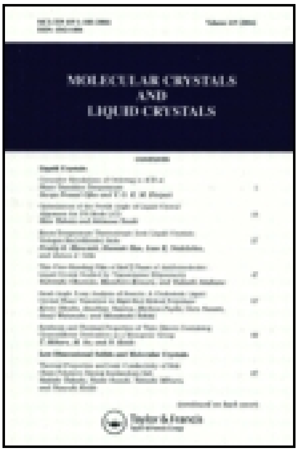

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Regio- and Enantio-Selective Photoreactions of Cyclohex-2-Enone, Coumarin and Acrylanilide as Inclusion Complexes with Optically Active Host Compounds

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REGIO- AND ENANTIO-SELECTIVE PHOTOREACTIONS OF CYCLOHEX-2-ENONE, COUMARIN AND ACRYLANILIDE AS INCLUSION COMPLEXES WITH OPTICALLY ACTIVE HOST COMPOUNDS

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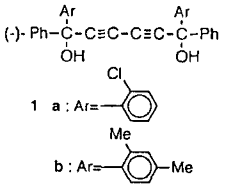
Abstract Regio- and enantio-selective photodimerization reactions of cyclohex-2-enone (**4**) and coumarin (**7**), and enantioselective photocyclization of acrylanilides (**12**, **16**, **18**, and **20**) in inclusion crystal with optically active host compounds (**1**, **2**, and **3**) are reported. X-ray structure studies of the inclusion crystal are also reported.

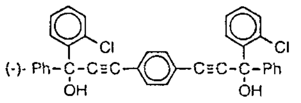
INTRODUCTION

when guest molecules are arranged together in the channel of a host-guest inclusion crystal, intermolecular reactions of the guest compound may proceed stereoselectively and efficiently. An enantioselective reaction is expected when optically active host compounds are used. According to this idea, photodimerization reactions of cyclohex-2-enone (**4**) and coumarin (**7**) in inclusion crystal with the optically active host compounds (**1**, **2**, and **3**) were studied. Enantioselective photocyclization of acrylanilides (**12**, **16**, **18**, and **20**) in inclusion crystal with the optically active host compounds was also studied. In order to know the mechanism of the selective photoreaction in inclusion crystal, X-ray structures of inclusion crystals were analyzed.

Regio- and enantio-selective photodimerization of 4

A solution of **2** (5 g, 9 mmol) and **4** (1.7 g, 18 mmol) in ether-hexane (1:1, 10 ml) was kept at room temperature for 6 h to give a 1:2 inclusion complex of **2** and **4** as colorless prisms (6 g, 90%), mp 90-95 °C. A suspension of the powdered complex (4.2 g) in a water (100 ml) containing a small amount of sodium alkylsulfate as surfactant was irradiated by using 100W high-pressure Hg-lamp at room temperature for 24 h. The reaction mixture was filtered, dried, and distilled in vacuo to give (-)-**5** in 48.0% ee as an oil (0.8 g, 75% yield).[1] Optically pure sample of the (-)-5 was easily obtained by complexation of the crude (-)-**5** of 48.0% ee with the optically active host **1a**. By the combination of the regio- and enatio-selective photodimerization of **4** in the inclusion complex with **2**, and the purification by the complexation with **1a**, finally gives optically pure **5**.[1] This result is in contrast to the photoreaction of **4** in benzene solution which gives a complex mixture of **5**, **6**, and unknown products.[2]





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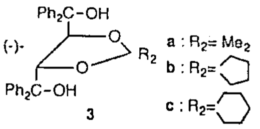

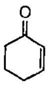

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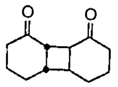

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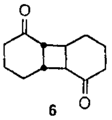

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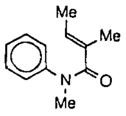

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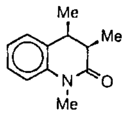

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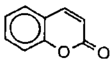

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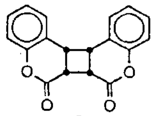

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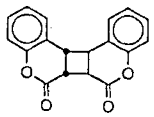

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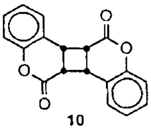

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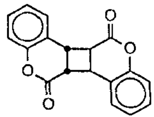

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<u>Regio- and enantio-selective photodimerization of **7**</u>

Photoreactions of **7** in EtOH both in the absence and in the presence of benzophenone as a sensitizer give, respectively, a mixture of syn-head-to-head dimer (**8**) and syn-head-to-tail dimer (**10**),[3] and anti-head-to-head dimer (9) together with a small amount of anti-head-to-tail dimer (**11**).[4] However, we found that photoirradiation of a 1:2 inclusion crystal of **1a** and of **1b** with **7** in the solid state gives **8** and **11**, respectively, in good yields.[5]

Interestingly, however, irradiation of a 1:1 inclusion crystal of **3a** with **7** prepared by recrystallization of the two components from ethyl acetate-hexane gave (-)-**9** of 96% ee, although the same irradiation of a 1:1 inclusion crystal of **3a** and **7** prepared by recrystallization from toluene-hexane gave **8**.[5]

Enantioselective photocyclization of 12, 16, 18, and 20

The photocyclization of acrylanilide to 3,4-dihydroquinolin-2(H)-one was first reported in 1971,[6] and its application to alkaloid synthesis has long been studied.[7] In this reaction, stereocontrol, especially enantiocontrol is important. We report almost perfect control of the photocyclization of acrylanilides (**12**, **16**, **18**, and **20**) to the corresponding, almost optically pure, 3,4-dihydroquinolin-2-ones, **14**, **17**, **19**, and **21**, respectively.

Irradiation of finely powdered 1:1 inclusion crystal of **3b** with **12** (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, (-)-**14** of 98% ee in 46% yield.[8] On the other hand, the same irradiation of a 1:1 inclusion crystal of **3c** with **7** gave (+)-**14** of 95% ee in 29% yield.[8] The striking enantiocontrol of the enantioisomeric hosts **3b** and **3c** to afford the (-)- and (+)-products, respectively, was also found in the photocyclization of **16**, **18**, and **20** (Table I). In the case of **20**, however, the optical yield of (+)-**21** was very low.

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

The selective photocyclization of **12** to **14** in the inclusion crystal with **3** can be interpreted as follows: of the two possible directions (S and R) in the conrotatory ring closure of the enol form (**12'**) of **12**, only the rotation towards the S direction, for example, occurs by control with the host **3b** (or **3c**) to give the intermediate **13**. The direction in which the conrotatory ring closure of **12'** occurs within the inclusion complex (**3b** of **3c**) should be determined by X-ray structure analysis. The 1,5-hydrogen shift on **13**, which probably proceeds in a suprafacial manner is also controlled precisely by the host **3** and finally gives trans-isomer **14**. When the irradiation of **12** was carried out in solution, a 1:1 mixture of racemic **14** and **15** was obtained. The enantioselective photocyclization of **16**, **18**, and **20** can also be interpreted in similar manner (Scheme 1). The stereochemistry of **19** was found to be trans.[9]

TABLE I Photocyclization of **12**, **16**, **18**, and **20** in 1:1 inclusion crystals with the hosts **3b** and **3c**

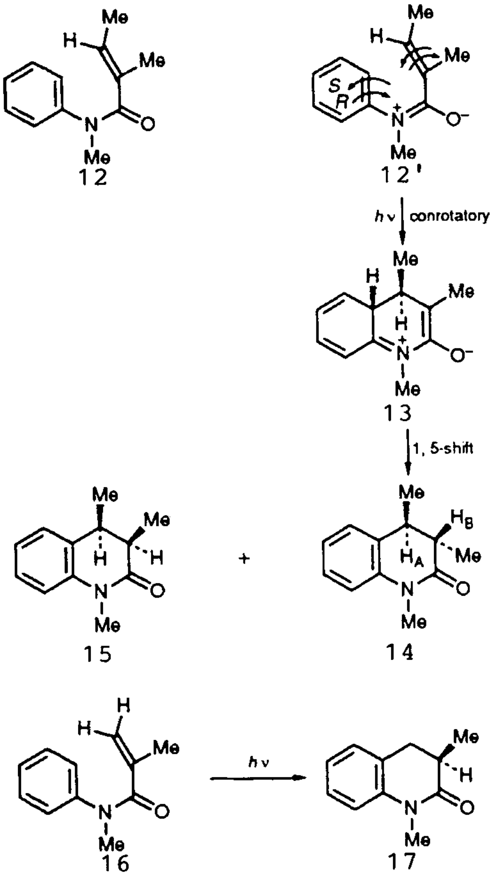
				Product	
Anilide	Host	Mp of complex/°C	Reaction time/h	Yield (%)[d]	Optical purity(%ee)
12	**3b**	95-98	150	(-)-**14** 46	98
12	**3c**	--[a]	150	(+)-**14** 29	95
16	**3b**	99-102	150	(-)-**17** 65	98
16	**3c**	--[a]	150[b]	(+)-**17** 44	98
18	**3b**	118-121	50[c]	(+)-**19** 62	70
18	**3c**	121-124	50[c]	(-)-**19** 29	99
20	**3b**	123-124	15[c]	(-)-**21** 64	98
20	**3c**	102	15[c]	(+)-**21** 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.

REFERENCES

1. K. Tanaka, O. Kakinoki and F. Toda, J. Chem. Soc. Perkin Trans. 1, 1992, 307.
2. E. Y. Y. Lam, D. Valentine and G. S. Hammond, J. Am. Chem. Soc., 89, 3482 (1989).
3. C. H. Claus, S. Farid and G. O. Schenck, Chem. Ber., 99, 625 (1966).
4. G. O. Schenck, I. von Wilucki and C. H. Kraus, Chem. Ber., 95, 1409 (1962).
5. K. Tanaka and F. Toda, J. Chem. Soc. Perkin Trans. 1, 1992, 943.

6. Y. Ogata, K. Takaki and I. Ishino, J. Org. Chem., 36, 3975 (1971).
7. I. Nonomiya and T. Naito, The Alkaloids, ed by A. Brossi (Academic Press, San Diego, 1983) vol XXII, p. 189; I. Ninomiya, T. Naito, T. Kiguchi and O. Miyata, Yukigousei Kagaku Kyokaishi, 48, 206 (1990).
8. K. Tanaka, O. Kakinoki and F. Toda, J. Chem. Soc., Chem. Commun., 1992, 1053.
9. I. Ninomiya, S. Yamauchi, T. Kiguchi, A. Shinohara and T. Naito, J. Chem. Soc. Perkin Trans. 1, 1990, 3207.



Scheme 1