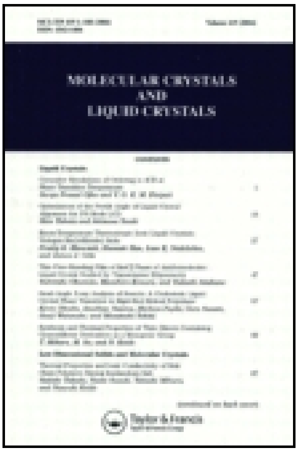

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Enantioselective Photoreaction in Inclusion Crystal

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ENANTIOSELECTIVE PHOTOREACTION IN INCLUSION CRYSTAL

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Abstract Mixing of powdered chiral hosts and achiral guest compounds gives inclusion complexes in which the latter molecules are arranged in a chiral form. Freezing of the chirality of the guest compounds by photoirradiation in the solid state gives optically active photoreaction products.

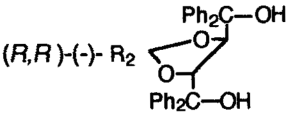
INTRODUCTION

Host-guest inclusion complexes are usually preapred by recrystallization of the host and guest compounds from solvent.[1,2] We found that mixing of powdered host and guest compounds in the absence of solvent also gives inclusion complexes.

RESULTS AND DISCUSSION

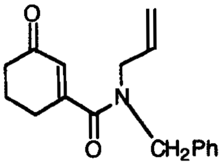
We have reported that irradiation of powdered 2:1 inclusion crystals of *(R,R)*-(-)-trans-2,3-bis(hydroxydiphenylmethyl)-1,4-dioxaspiro[4.4]nonane (**1b**)[3,4] and *N*-allyl-*N*-benzyl-3-oxo-1-cyclohexenecarboxamide (**2**) which had been prepared by recrystallization of these from ether, in a water suspension which contains alkylsulfate as a surfactant at room temperature for 10 h gave (-)-**3** of 100% ee in 90% yield.[5] The photoreaction of **2** itself in MeCN gives a mixture of *rac*-**3** and an isomeric photocycloaddition product.[6]

We found that the same inclusion complex of **1** and **2** as that prepared by recrystallization can be obtained just by mixing **1** and **2** in the solid state and that photoirradiation of the inclusion crystals obtained by mixing gives optically active photoreaction product.



1

a : R=Me
b : R_2= -$(CH_2)_4$-
c : R_2= -$(CH_2)_5$-



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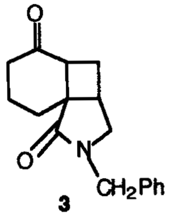

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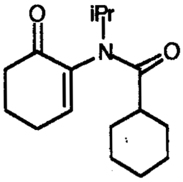

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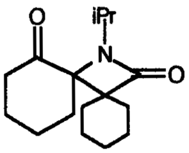

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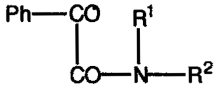
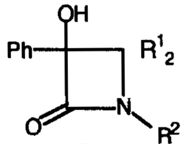


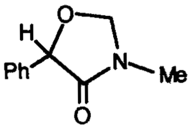
6

a : $R^1 = R^2 = Me$
b : $R^1 = Me$; $R^2 = iPr$
c : $R^1 = Et$; $R^2 = iPr$
d : $R^1 = nPr$; $R^2 = iPr$
e : $R^1 = R^2 = iPr$



7

a : $R^1 = H$; $R^2 = Me$
b : $R^1 = H$; $R^2 = iPr$
c : $R^1 = Me$; $R^2 = Et$
d : $R^1 = Me$; $R^2 = nPr$
e : $R^1 = Me$; $R^2 = iPr$



8a

For example, an occasional mixing of powdered **1b** of about 50-100 mm diameter and a half molar amount of oily **2** using an agate mortar and pestle for 1 h in order to avoid solidification gave the IR spectroscopically identical 2:1 inclusion complex crystal of **1b** and **2** with that obtained by the recrystallization method. Photoirradiation of the complex in a water suspension for 10 h gave (-)-**3** of 99% ee[7] in 48% yield. Such molecular movement in the solid state and arrangement in a chiral form are not special for **2** but are rather common. For example, mixing of powdered **1b** and an equimolar amount of powdered *N*-isopropyl-*N*-2-(1-oxocyclo-hex-2-enyl)cyclohexanecarboxamide (**4**) followed by irradiation gave the photocyclization product (-)-**5** of 81% ee in 37% yield. Photoirradiation of **4** in acetone gives *rac*-**5** together with an isomeric photocycloaddition product.[8]

N,N-Dialkylphenylglyoxylamide **6** also forms an inclusion complex on mixing with **1** and the achiral molecules of **6** are arranged in a chiral form in the inclusion crystal, even though such complexes are not obtained by recrystallization. When powdered *(R,R)*-(-)-trans-4,5-bis(hydroxydiphenylmethyl)-2,2-dimethyl-1,3-dioxacyclopentane (**1a**)[3,4] (2.8 g, 6 mmol) and oily *N,N*-dimethylphenylglyoxylamide (**6a**) (0.53 g, 3 mmol) were mixied for 1 h by using agate mortar and pestle, the mixture was solidified to give a 2:1 inclusion omplex crystal of **1a** and **6a** (3.33 g). A chiral arrangement of the achiral **6a** molecules in the inclusion complex was proven by photoreaction which gives optically active β-lactam. A suspension of powdered 2:1 complex of **1a** and **6a** (3.2 g) in water (50 ml) suspension for 10 h gave (+)-2-hydroxy-1-methyl-2-phenylazetidin-2-one **7a** with 61% ee (0.3 g, 70% yield). The inclusion complex of **1a** and **6a** could not obtained by recrystallization, although more than 15 organic solvents were tested. In all cases, **1a** crystallised out separately.

On the other hand, *(R,R)*-(-)-trans-2,3-bis(hydroxydiphenylmethyl)-1,4-dioxaspiro-[4.4]nonane (**1b**)[3,4] formed a 1:1 inclusion complex with **6a** either by mixing in the solid state or by recrystallization from diethyl ether. Photoirradiation of these inclusion complexes in a water suspension gave (-)-**7a** and (-)-3-methyl-5-phenyloxazolidin-4-one **8a** in the optical and chemical yields reported in Table 1. Optical and chemical yields are comparable by either preparative method.

Infrared spectra in Nujol mulls of these inclusion complexes prepared either by mixing or recrystallization are identical. Furtehrmore, irradiation of a concentrated solution of **1b** (3.33 mmol) and **6a** (3.33 mmol) in diethyl ether (50 ml) for 10 h under stirring gave *rac*-**7a** in 10% yield and *rac*-**8a** in 66% yield. These data clearly show that the same inclusion complex is obtained by either mixing or recrystallization.

A similar chiral host, *(R,R)*-(-)-trans-2,3-bis(hydroxy-diphenylmethyl)-1,4-dioxaspiro[5.4]decane (**1c**)[3,4] also formed a 2:1 inclusion complex with **6a** by the mixing and recrystallization method, however, photoirradiation of these two complexes in a water suspension gave (+)-**7a** and (-)-**7a**, respectively (Table 1), although the optical yield of the (-)-**7a** was higher than that of (+)-**7a**. It is very interesting that direction of the chiral arrangemnt of **7a** in the complex with **1c** changes depending on the preparation method used.

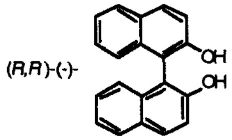
This result is very interesting not only from the viewpoint of synthetic potential but also in terms fundamental molecular behavior. Thus, one can obtain both enantiomeric photoreaction products by using a single optically active host compound; and it is clearly of interest that the molecular assembly of host and guest compounds occurs in a different manner in the solid state and in solition.

The chiral host compounds, *(R,R)*-(+)-2,2'-dihydroxy-1,1'-binaphthyl (**9**),[1,2] *(S,S)*-(-)-1,4-bis[3-(*o*-chlorophenyl)-3-hydroxy-3-phenyl-1-propynyl]-benzene (**10**)[9] and (S)-

TABLE 1 Formation of optically active **7a** and **8a** by irradiation for 10 h of the inclusion complex of chiral host compounds and **2a** prepared by mixing in the solid state and recrystallization from toluene

host	host: guest	product from the complex prepared by mixing (yield (%), optical purity (% ee))		product from ther complex prepared by recrystallisation (yield (%), optical purity (% ee))	
1a	2:1	(+)-**7a** (70, 61)	—	—	—
1b	1:1[a]	(-)-**7a** (29, 82)	(-)-**8a** (35, 45)	(-)-**7a** (47, 79)	(-)-**8a** (23, 42)
1c	2:1	(+)-**7a** (48, 41)	—	(-)-**7a** (39, 85)	—
9	2:1[b]	(+)-**7a** (22, 4)	(-)-**8a** (19, 49)	—	—
10	2:1	(-)-**7a** (44, 14)	—	—	—
11	2:1[c]	(-)-**7a** (27, 36)	—	—	—

[a] Diethyl ether was used for complexation by recrystallization. [b] Irradiated for 10 days.
[c] Irradiated for 5 days.



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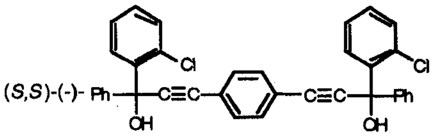

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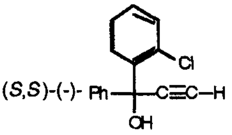

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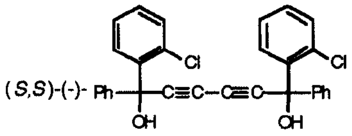

12

(-)-1-(*o*-chlorophenyl)-1-phenyl-2-propyn-1-ol (**11**)[10] formed a 2:1 inclusion complex with **6a** only by mixing. Photoirradiation of an aqueous suspension of these inclusion complexes gave optically active **7a** and **8a** (Table 1) although enantiomeric excess was not so as for **1a**.

Previously we have reported formation of a host-guest complex by mixing both components in the solid state.[11] However, this is the first example of the formation of host-guest complexes by mixing which can not be obtained by recrystallization and of the chiral arrangement of achiral molecules in the complex formed on mixing.

Chiral arrangement of **6a** molecules in an inclusion crystal with (*S,S*)-(-)-1,6-di(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol (**12**)[12] also depends on the conditions of the inclusion complexation experiment. Recrystallization of **12** and **6a** from ether gives a 1:1 inclusion complex, which upon irradiation affords (-)-**7a** of 100% ee in quantitative yield.[13] X-ray structure study of the inclusion complex showed that **6a** is arranged in a chiral form.[13] However, irradiation of the inclusion crystal prepared by mixing **8** and **6a** gave *rac*-**7a**. In the latter crystal, **6a** molecules would not be arranged in a chiral form. Interestingly, however, both inclusion crystals are thermally interconvertible. After melting (mp 126-127 °C), the former is solidified by cooling to give the latter, but the latter is converted to the former by heating gradually and melts again at 126-127 °C.

It has been reported that **6e** forms chiral crystals in which **6e** molecules are arranged in a chiral form produced by a 90° twisting around the single bond between two CO groups,[14] and that irradiation of the chiral crystals gives optically active **7e** of 93% ee in 74% yield.[15] This time, we found that **6c** also forms chiral crystals which upon irradiation gives optically active **7c**. Although **6e** forms inclusion crystals neither with **1** nor **8**, **6c** forms an inclusion complex with **1** both by recrystallization and solid state complexation procedures. Especially, 1:1 inclusion crystals of **1c** with **6c** are easily obtained by mixing a 2:1 MeOH complex (**9**) of **1c** and **6c**. The complexation in the solid state can be followed by its IR spectrum. As the complexation proceeds, hydrogen bonded υOH absorption between **1c** and MeOH (3550 cm^{-1}) decreases and finally disappears, and a new hydrogen bonded υOH absorption between **1c** and **6c** (3250 cm^{-1}) appears and increases (Figure 1). The complexation was completed within 4 h. Irradiation of the resulting inclusion complex (**14**) of **1c** with **6c** gave (+)-**7c** of 76% ee.

Very interestingly, by mixing powdered **13** and powdered (-)-crystals of **6c**, 1:1 inclusion crystals of **1c** and (+)-**6c** were formed. Firstly, (-)-crystals of **6c** were prepared in large quantity by adding one piece of a (-)-crystal of **6c** as a seed crystal during recrystallization of **6c** from ether. Photoirradiation of powdered (-)-crystals of **6c** in the solid state gave (-)-**7c** of 80% ee in 54% yield. Secondly, a 1:1 inclusion complex of **13** and (+)-**6c** (**14**) was obtained by mixing powdered **13** and (-)-crystals of **6c**. The (+)-

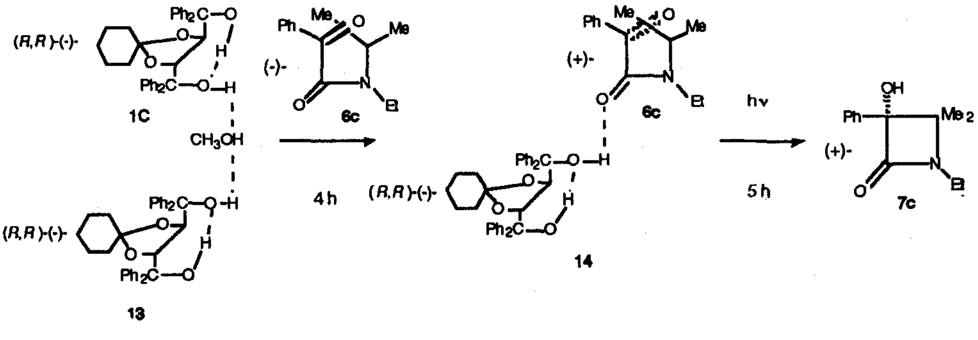

FIGURE 1 Conversion of the chirality of **6c** through inclusion complexation.

arrangement of **6c** molecules in **14** can be proven by its photoirradiation in a water suspension for 5 h which gives (+)-**7c** of 76% ee in 72% yield. Interconversion between the molecular arrangement of **6c** in the (-)- and (+)-forms easily occurs by the complexation with chiral host **1** in the solid state. In other words, molecules move easily in the solid state and change their chiral arrangement according to the chiral circumstances in the crystal.

ACKNOWLEDGMENT

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