Chiral Arrangement of *N*-Ethyl-*N*-isopropylphenylglyoxylamide Molecule in Its Own Crystal and in an Inclusion Crystal with a Host Compound and Their Photoreactions in the Solid State That Give Optically Active *β*-Lactam Derivatives. X-ray Analytical and CD Spectral Studies

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N-Ethyl-*N*-isopropylphenylglyoxylamide (**3c**) forms chiral crystal in which its achiral molecules are arranged in a chiral form, and the chirality in the crystal was identified by measurement of the CD spectrum in Nujol mull. Generation of the chirality occurs by twisting of the CO−CO bond of **3c** in the crystal. Photoirradiation of the chiral crystal of **3c** in the solid state gave optically active *β*-lactam derivative (**4c**) of 80% ee. By X-ray analysis, absolute configurations of the chiral crystal and **4c** were elucidated. The achiral molecules of **3c** are also arranged in chiral forms in inclusion complexes with chiral hosts such as (*R*,*R*)-(−)-*trans*-2,3-bis(hydroxydiphenylmethyl)-1,4-dioxaspiro[4.4]nonane (**5a**), (*R*,*R*)-(−)-*trans*-2,3-bis(hydroxydiphenylmethyl)-1,4-dioxaspiro[5.4]-decane (**5b**), and their (*S*,*S*)-(+)-enantiomers, **6a** and **6b**, respectively. The crystal structure of a 1:1 inclusion complex of **3c** with **5b** (**7b**) was analyzed. Photoirradiation of **7b** in the solid state gave (*R*)-(+)-**4c** of 85% ee. Photochemical conversions of some other derivatives of **3c** to the corresponding *β*-lactams were also studied. Interestingly, however, irradiation of the 1:1 inclusion complex of *N*,*N*-dimethylglyoxylamide (**3a**) with **5a**, which had been prepared by mixing both components in the absence of solvent, gave (*R*)-(+)-*β*-lactam (**9a**) of 45% ee, although the 1:1 complex that had been prepared by recrystallization of the components from toluene gave (*S*)-(−)-**9a** of 100% ee. Mixing of powdered chiral (−)-**3c** crystal with a 2:1 inclusion complex of **5b** and MeOH gave a new 1:1 complex of **5b** and chiral (+)-**3c**. The inversion of the chirality of **3c** in the solid state was studied by continuous measurements of CD spectra in Nujol mulls.

Introduction

Various kinds of achiral compounds form chiral crystals in which the achiral molecules are arranged in a chiral form. Freezing of the chirality in the crystal by chemical reaction is a goal of absolute chiral synthesis. It would be very beneficial to be able to carry out chiral synthesis without using any chiral auxiliary and is interesting in relation to the origin of optically active compounds on the earth.[1] In view of these points, some research groups have been searching for appropriate methods to achieve chiral synthesis in the crystalline state, and several successful syntheses of optically active compounds by photoreactions of chiral crystals have been reported. For example, *β*-lactam derivatives have been formed from oxoamide,[2a−d] amide,[3a,b] and thioamide,[4] oxetane from amide,[5] *γ*-butyrolactone from diketone,[6] and cyclopropane derivatives from olefins.[7a−c] These are all

intramolecular photocyclization reactions. However, recently chiral synthesis by photoreaction between two different molecules that are arranged in a chiral form in a crystal has also been reported.[8]

We report here formation of a chiral crystal of the title oxoamide (**3c**) and photochemical conversion of the chiral crystal to optically active *β*-lactam (**4c**). We also report that the chiral configuration of **3c** in its own chiral crystal is easily converted to the other configuration in the solid state in the presence of a chiral host compound, and their new inclusion complex is constructed. These dynamic molecular behaviors in the solid state were detected by continuous measurment of CD spectra in Nujol mull. Absolute configurations of the chirally ordered molecule of **3c** in the chiral crystal and of the *β*-lactam **4c** were determined by X-ray analysis.

Results and Discussion

The phenylglyoxylamide **3c** was prepared as colorless crystals, mp 62−64 °C, from benzoylformyl chloride (**1**)

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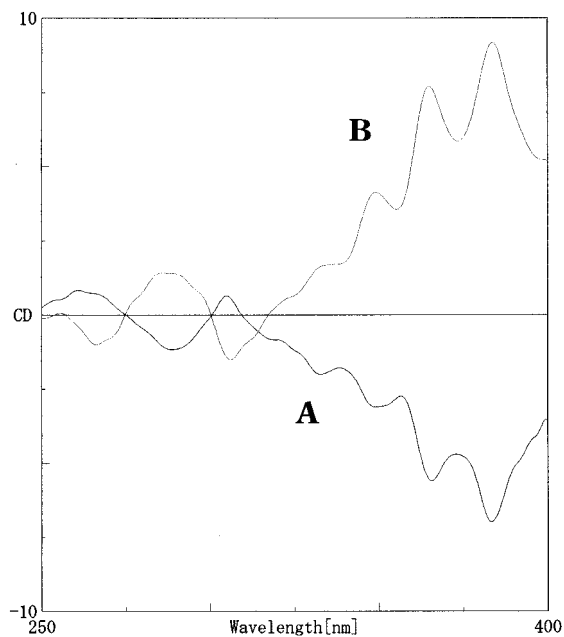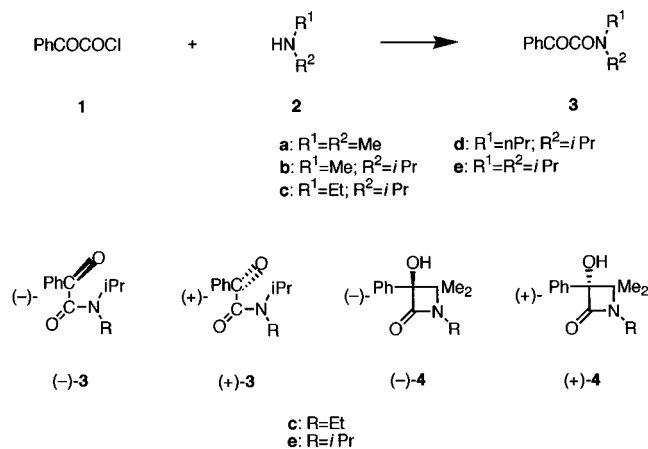
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Figure 1. CD spectra in Nujol mulls of (*S*)-(−)- (A) and (*R*)-(+)-**3c** crystal (B).

Figure 2. X-ray structure of (*R*)-(+)-**3c** crystal, which gives (R-)-(+)-**4c** upon irradiation.

Figure 3. X-ray structure of (*R*)-(+)-**4c**.

(*R*)-(+)-**3c** was carried out. As shown in Figure 2, the molecule of **3c** becomes chiral by twisting around the single bond C7−C8 between the two CO groups, and the isopropyl group is located in a position near the benzoyl carbonyl, C7=O1. The analysis also revealed that due to conformational restriction introduced by bicarbonyl unit, the central carbon atom of the isopropyl group and the carbon atom from benzoyl group are in close proximity (3.51 Å), permitting easy β-lactam ring closure. Moreover, inspection of the Cambridge Crystallographic Database showed that among 23 molecules containing the NCOCOC unit, the distance between terminal C and N atoms is shorter than 3.55 Å in 14 cases. Conformational restriction was manifested in that case by the value of the N−C−C−C tortion angle limited to the range +80−120°.

The steric course of the photocyclization of **3c** to **4c** was studied by X-ray structure analysis of **4c** (Figure 3). The absolute configuration and steric course of the photocyclization of the (*R*)-(+)-**3c** was further confirmed by an internal reference method using a 1:1 inclusion complex (**7b**) of (*R*)-(+)-**3c** with (*R*,*R*)-(−)-*trans*-2,3-bis-(hydroxydiphenylmethyl)-1,4-dioxaspiro[5.4]decane (**5b**)[10a] (Figure 4). The molecule of (*R*)-(+)-**3c** is included by forming an intermolecular hydrogen bond between the

a: R^1=R^2=Me   d: R^1=nPr; R^2=*i*Pr
b: R^1=Me; R^2=*i*Pr   e: R^1=R^2=*i*Pr
c: R^1=Et; R^2=*i*Pr

c: R=Et
e: R=*i*Pr

and *N*-ethyl-*N*-isopropylamine (**2c**). The chirality of each crystal of **3c** was easily detected by measurement of their CD spectra in Nujol mulls[9] as shown in Figure 1. The chiral crystals that give (*S*)-(−)-**4c** and (*R*)-(+)-**4c** by photoirradiation are tentatively termed as (*S*)-(−)-**3c** and (*R*)-(+)-**3c** crystals, respectively. When one piece of (*S*)-(−)-**3c** crystal was added as a seed crystal during the recrystallization of **3c** from ether, a large quantity of (*S*)-(−)-**3c** crystal was obtained easily. Of course, recrystallization of the (*S*)-(−)-**3c** crystal from ether by adding one piece of (*R*)-(+)-**3c** crystal as a seed crystal gave (*R*)-(+)-**3c** crystal in large quantitity. Irradiation of powdered (*S*)-(−)- and (*R*)-(+)-**3c** crystal gave (*S*)-(−)- and (*R*)-(+)-**4c** of 80% ee, respectively, in 55% yield. In the photoreaction, only the isopropyl group of **3c** reacted and no other compound produced by photoreaction of the ethyl group was detected.

In order to know why only the isopropyl group reacts and how the molecules of **3c** are arranged in a chiral form in their own crystal, X-ray crystal structure analysis followed by determination of absolute configuration of
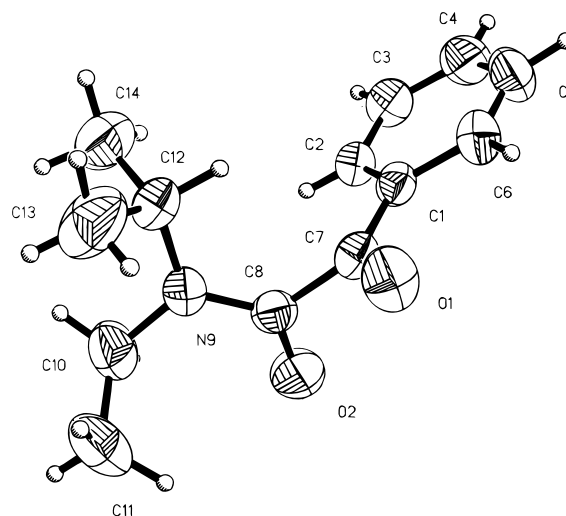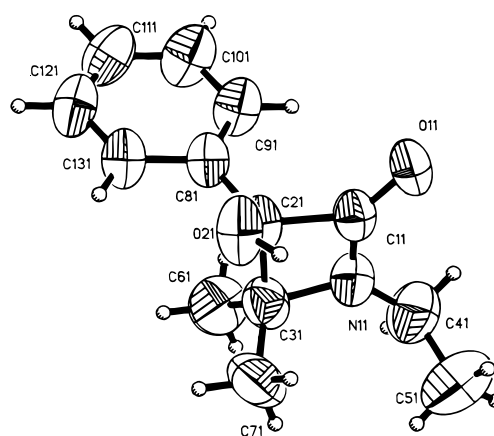
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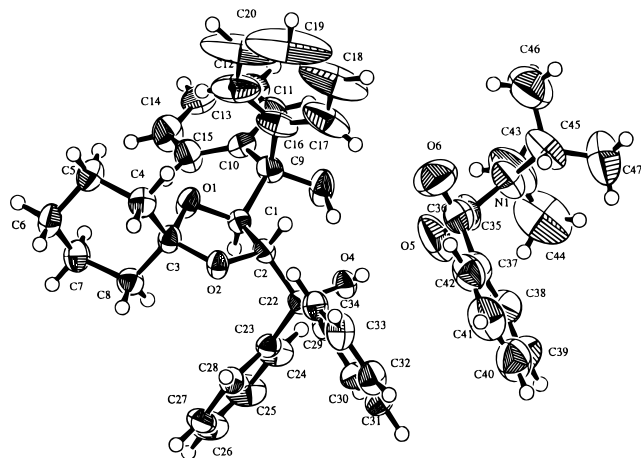
Figure 4. X-ray structure of a 1:1 inclusion complex (**7b**) of (*R*)-(+)-**3c** with **5b**.

C35=O5 carbonyl group of **3c** and the O4−H2 hydroxyl group of **5b** with an O5---O4 distance of 2.72 Å. The other remaining O3−H1 hydroxyl group of **5b** also forms an intramolecular hydrogen bond with the O4−H2 hydroxyl oxygen, and the distance between O3 and O4 is 2.67 Å. The absolute configuration of (*R*)-(+)-**3c** included in **7b** (Figure 4), assigned by the (*R*,*R*) absolute configuration of the host **5b** as the internal reference, was consistent with that of the host-free (*R*)-(+)-**3c** (Figure 2), giving further confirmation of the absolute configuration. In crystals of both (*R*)-(+)-**3c** and its inclusion complex **7b** with **5b**, the chirality of the molecules of **3c** is generated by a similar chiral conformation due to the twisting around the single bond of CO−CO. Irradiation of **7b** in the solid state gave (*R*)-(+)-**4c** of 85% ee in 37% yield as the sole product. The reaction mechanism can be explained as follows. The O6 carbonyl oxygen of (*R*)-(+)-**3c** excited by the irradiation abstracts the nearest H3 hydrogen atom of the isopropyl group over the O6---H3 distance of 2.74 Å to form a hydroxyl group. Next, a radical coupling occurs between the C36 and C45 radicals due to the short distance of 2.84 Å, resulting in the formation of (*R*)-(+)-**4c**. Similarly, irradiation of a 1:1 inclusion complex (**7a**) of (*R*)-(+)-**3c** with (*R*,*R*)-(−)-*trans*-2,3-bis(hydroxydiphenylmethyl)-1,4-dioxaspiro[4.4]-nonane (**5a**)[10a,b] afforded (*R*)-(+)-**4c** of 87% ee in 31% yield.

5   **6**

a: n=0 , **b**: n=1
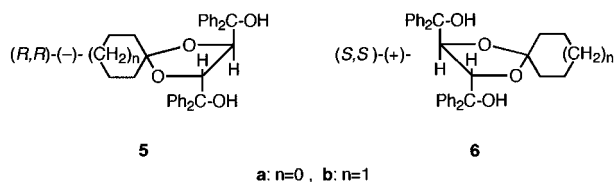
By a similar inclusion complexation with chiral host compound, achiral oxoamide molecules are arranged in a chiral form and irradiation of the inclusion complex gives optically active β-lactam derivative. For example, irradiation of a 1:1 inclusion complex of oily *N,N*-dimethylphenylglyoxylamide (**3a**) with (*S,S*)-(−)-1,6-di-(*o*-chlorophenyl)-1,6-diphenylhexa-1,4-diyne-1,6-diol (**8**)[11] gives (*S*)-(−)-**9a** of 100% ee in quantitative yield.[12] X-ray

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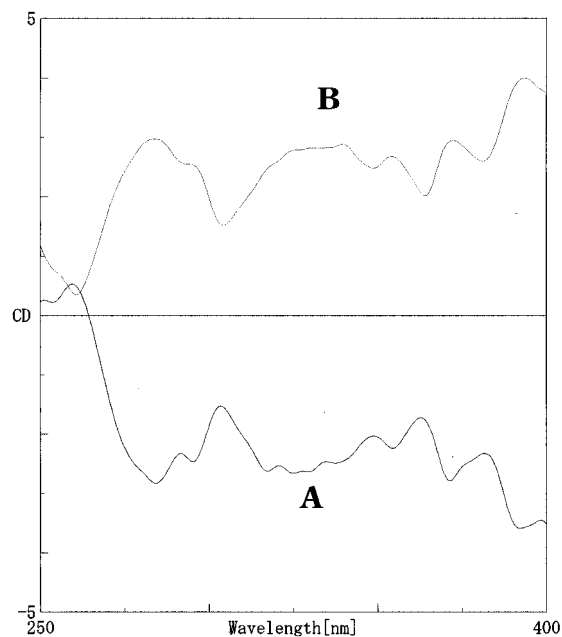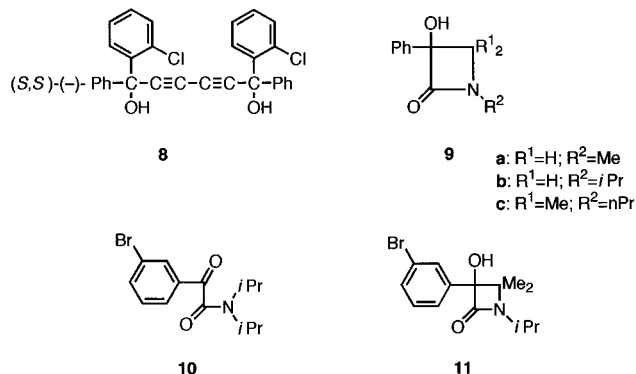(12) Kaftory, M.; Yagi, M.; Tanaka, K.; Toda, F. *J. Org. Chem.* **1988**, *53*, 4391.

Figure 5. CD specta of (*S*)-(−)- (A) and (*R*)-(+)-**3e** (B).

structure analysis of the complex showed that the achiral glyoxylamide molecule is arranged in a chiral form due to a similar twisitng of the CO−CO bond.[12]

(*S,S*)-(−)- **8**

9   **a**: R^1=H; R^2=Me
       b: R^1=H; R^2=*i*Pr
       c: R^1=Me; R^2=nPr

10   **11**

As mentioned above, the chiral arrangement of achiral molecule in a crystal can easily be detected by CD spectral measurement in Nujol mull, and (*S*)-(−)- and (*R*)-(+)-**3c** crystals showed CD spectra of a mirror-imaged relation (Figure 1). Similarly, (*S*)-(−)- and (*R*)-(+)-chiral crystals of **3e** showed the CD spectra of similar mirror-imaged relation (Figure 5). Since β-lactams **4** and **9** have no benzoyl chromophore any more, their characteristic bands become weaker as the photoconversion of **3** to the β-lactam proceeds. The photoconversion of the *m*-bromophenyl derivative of **3e** (**10**), which shows relatively strong CD absorptions to the corresponding β-lactam (**11**),[13] was followed by the CD spectral measurement. As shown in Figure 6, CD spectra of the chiral crystal of **10** in Nujol mull turn to the weak absorptions of **11** as the photoreaction proceeds. It is also very interesting that the solid-state photoreaction proceeds efficiently in Nujol mull. This is not a solution reaction in liquid paraffin because the achiral molecules of **3c**, **3e**, and **10** can exist in a chiral form only in the crystalline state but not in solution. Photoreactions of **3c**, **3e**, and **10** in solution give *rac*-products.

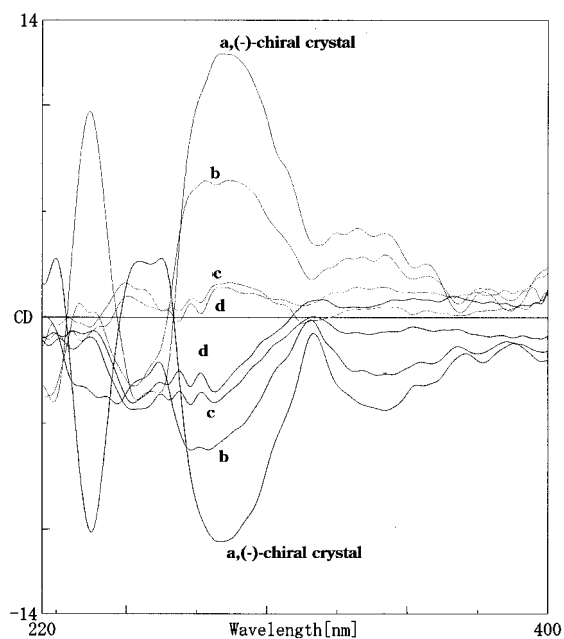(13) Toda, F.; Miyamoto, H. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1129.

Figure 6. Photoconversion of (+)- and (−)-chiral crystals of **10** to (+)- (A) and (−)-**11**(B), respectively, by continuous measurements of CD spectra in Nujol mulls, after (a) 0 min, (b) 2 min, (c) 4 min, and (d) 6 min of irradiation.

Easy conversion of (*S*)-(−)-**3c** to (*R*)-(+)-**3c** in the solid state was observed during an inclusion complexation experiment of the former with **5b**. By mixing powdered 2:1 inclusion complex of **5b** with MeOH (**12**) with twice the molar amount of powdered (*S*)-(−)-**3c** for 4 h at room temperature, a new 1:1 inclusion complex of (*R*)-(+)-**3c** with **5b** was formed (Scheme 1). Irradiation of the newly formed complex gave (*R*)-(+)-**4c** instead of (*S*)-(−)-**4c**, although irradiation of (*S*)-(−)-**3c** gives (*S*)-(−)-**4c**. This result shows that the configuration of (*S*)-(−)-**3c** was converted to (*R*)-(+)-**3c** during the inclusion complexation with **5b** by mixing in the solid state. This conversion would occur due to the following reasons: (a) the system becomes thermodynamically more stable by the inclusion complex formation of (*R*)-(+)-**3c** with **5b**, and (b) since **5b** includes (*R*)-(+)-**3c** but not (*S*)-(−)-**3c**, the latter should be converted to the former before the inclusion complexation. It has also been well established that inclusion complexation occurs efficiently in the solid state.[14] The conversion of (*S*)-(−)-**3c** into (*R*)-(+)-**3c** during the complexation in the solid state was observed by continuous measurement of CD spectra in Nujol mull (Figure 7). As the complexation proceeds, strong CD spectra of the (−)-Cotton effect due to (*S*)-(−)-**3c** are gradually converted to the spectra of the (+)-Cotton effect of (*R*)-(+)-**3c**. These spectra are attributed to the chirality of **3c** because **5b** does not show a clear CD spectrum.

Some other *N*,*N*-dialkylphenylglyoxylamides also form inclusion complexes on mixing with **5** or **6**, and the achiral molecules of these glyoxylamides are arranged in a chiral form in the inclusion crystal. Mixing of oily **3a** with an equimolar amount of powdered **5a** or **6a** for 30 min followed by irradiation in the solid state with occasional mixing for 30 h gave (−)-**9a** of 78% ee (54%) or (+)-**9a** of 65% ee (50%), respectively, in the yields indicated. Similar treatment of oily **3b** with **5a** or of oily **3d** with **5b** followed by photoirradiation gave (−)-**9b** of

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87% ee (45%) or (−)-**9c** of 93% ee (39%), respectively, in the yields indicated.

Very interestingly, irradiation of the 1:1 inclusion complex (**13**) of **3a** with **5b**, which had been prepared by mixing both components in the absence of solvent, gave (+)-**9a** of 45% ee in 42% yield, although the same irradiation of the complex (**14**) prepared by recrystallization of **3a** and **5b** from toluene gave the other enantiomer (−)-**9a** of 100% ee in 40% yield. The type of chiral arrangement of **3a** molecules varies depending on the conditions of the inclusion complexation experiment. The chiral arrangement of **3a** in **13** and **14** in an opposite type was detected by measurement of their CD spectra in Nujol mull (Figure 8). Nevertheless, both the inclusion complexations of **3a** with **5a** by the mixing and recrystallization methods gave the same 1:1 complex, which gives (−)-**9a**.

Chiral arrangement of **3a** in an inclusion crystal with **8** also depends on the conditions of the inclusion complexation experiment. As described above, irradiation of the 1:1 inclusion complex that had been prepared by recrystallization of the component from ether gave (−)-**9a** of 100% ee in quantitative yield.[12] X-ray structural study of the inclusion crystal showed that **3a** molecules are arranged in the chiral form, which gives (−)-**9a** by the photoreaction. On the other hand, irradiation of the inclusion crystal prepared by mixing **3a** and **5a** gave *rac*-**9a**. 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.

Conclusions

It was established that glyoxylamide **3c** forms a chiral crystal in which achiral molecules of **3c** are arranged in a chiral form, and its irradiation in the solid state gave optically active β-lactam **4c**. The achiral molecules of **3c** are also arranged in a chiral form in its inclusion complex crystal with a chiral host such as **5a** or **5b**, and irradiation of the complex gave optically active β-lactam. The chiral arrangement of **3c** in the chiral crystal and in the inclusion crystal were also proven by X-ray analysis. Absolute configuration of the chirally arranged **3c** and the β-lactam **4c**, which was derived from **3c**, was determined by X-ray analysis. It was also found that the chiral order of the achiral molecule of **3c** can be easily detected by measurement of CD spectrum of powdered crystal in Nujol mull. By mixing (*S*)-(−)-**3c** crystal and a 2:1 inclusion complex crystal of **5b** and MeOH, a new 1:1 inclusion complex of (*R*)-(+)-**3c** and **5b** was formed and irradiation of the complex gave (*R*)-(+)-**4c**. During the mixing, (*S*)-(−)-**3c** is converted to (*R*)-(+)-**3c** and is included with **5b** to give a new 1:1 inclusion complex with **5b**. The conversion of the chirality of (*S*)-(−)-**3c** to the opposite one (*R*)-(+)-**3c** in the solid state can be followed by continuous measurement of the CD spectra in Nujol mull. These data suggest that molecules easily move enantioselectively and order selectively in the solid state. Interestingly, chirality of **3a** in the inclusion complex with **5b**, which had been prepared by recrystallization of the components from toluene, was found to be just opposite to that in the complex that had been prepared by mixing of both components in the solid state. These opposite chiralities were measured by CD spectroscopy.
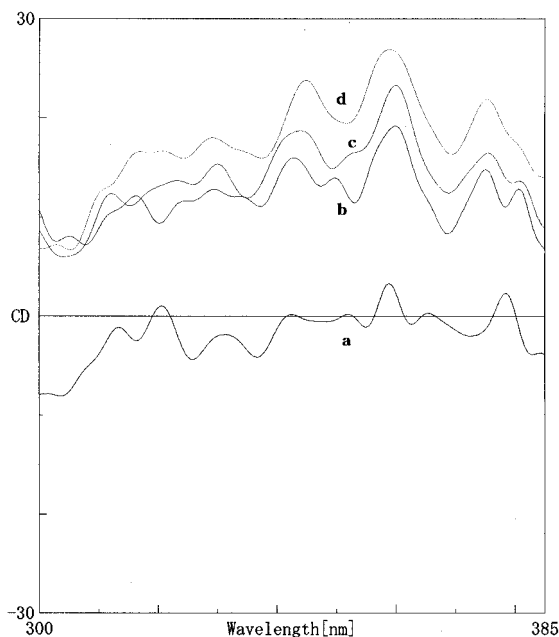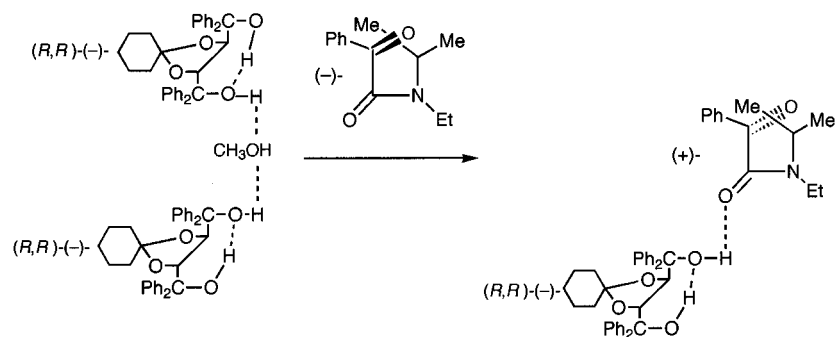
Scheme 1

Figure 7. CD spectra of a mixture of (*S*)-(−)-**3c** crystal (1 mg), a 2:1 inclusion complex of **5b** with MeOH (**12**) (3 mg), and liquid paraffin (10 mg) after (a) 0 min, (b) 30 min, (c) 60 min, and (d) 180 min in the preparation of the Nujol paste sample.
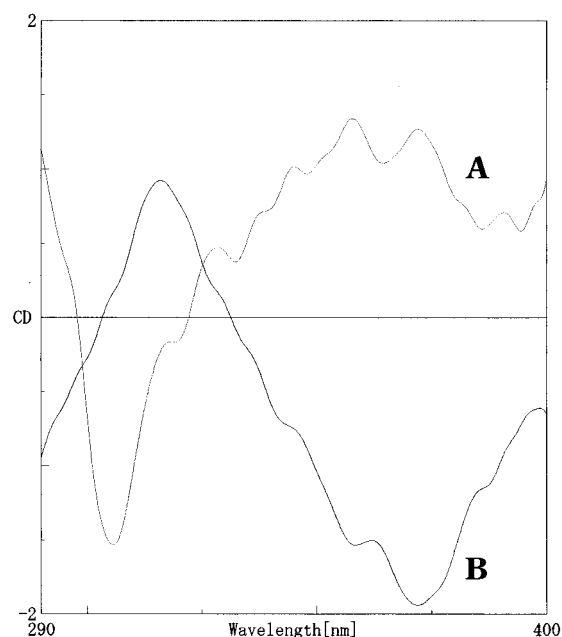

Figure 8. CD spectra of 1:1 inclusion complexes of **3a** with **5b** that were prepared by mixing in the absence of solvent (A) and recrystallization from toluene (B) of both components.

Experimental Section

Preparation of 3c. To an ice-cooled solution of *N*-ethyl-*N*-isopropylamine (6 g, 60 mmol) and triethylamine (30 mL) in dry ether (60 mL) was added a solution of benzoylformyl chloride[14] (10 g, 60 mmol) in dry ether (10 mL), and the mixture was stirred for 3 h in an ice bath. After filtration of triethylammonium hydrochloride, the filtrate was washed with dilute HCl and aqueous NaHCO$_3$ and dried over MgSO$_4$. The crude product obtained by evaporation of the solvent was chromatographed on silica gel using toluene−AcOEt (4:1) and recrystallized from ether to give **3c** as colorless prisms (4.2 g, 32% yield, mp 62−64 °C): IR 1675 and 1630 cm^{-1} (C=O); ^{1}H NMR δ 1.20 (d, *J* = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.36 (t, *J* = 7 Hz, 3H, CH$_2$C*H*$_3$), 3.46 (q, *J* = 7 Hz, 2H, C*H*$_2$CH$_3$), 3.70−3.83 (m, 1H, C*H*(CH$_3$)$_2$), 7.49−7.95 (m, 5H, Ph). Anal. Calcd for C$_{13}$H$_{17}$O$_2$N: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.10; H, 8.05; N, 6.33.

Preparation of Chiral Crystals of (−)- and (+)-3c. The chirality of each crystal of **3c** can be determined by CD spectral measurement in Nujol mull (Figure 1). When one piece of (*S*)-(−)-**3c** or (*R*)-(+)-**3c** crystal was added during the recrystallization of **3c** from ether, (*S*)-(−)-**3c** or (*R*)-(+)-**3c**, respectively, was obtained in large quantity.

Irradiation of (*S*)-(−)- and (*R*)-(+)-3c Crystals in the Solid State. After irradiation of powdered (*S*)-(−)- or (*R*)-(+)-**3c** (0.4 g) for 50 h, crude product was purified by column chromatography on silica gel using toluene−AcOEt (4:1) as eluent to give (*S*)-(−)- or (*R*)-(+)-**4c** of 80% ee, respectively, as

colorless needles (0.22 g, 55% yield, mp 139−141 °C, [α]$_D$ −40° (*c* 1.9, MeOH). By recrystallization from ether, (*S*)-(−)- and (*R*)-(+)-**4c** of 100% ee were obtained easily: IR 3215 (OH) and 1735 cm^{-1} (C=O); ^{1}H NMR δ 0.97 (s, 3H, CH$_3$), 1.26 (t, *J* = 7 Hz, 3H, CH$_2$C*H*$_3$), 1.50 (s, 3H, CH$_3$), 3.23 (s, 1H, OH), 3.22−3.31 (m, 2H, C*H*$_2$CH$_3$), 7.31−7.41 (m, 5H, Ph). Anal. Calcd for C$_{13}$H$_{17}$O$_2$N: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.38; H, 8.15; N, 6.34.

Preparation of Inclusion Complex of (*R*)-(+)-3c with 5a and 5b. When a solution of **3c** (1.5 g, 6.8 mmol) and **5a** (3.37 g, 6.8 mmol) in ether (10 mL) was kept at room temperature for 12 h, a 1:1 inclusion complex (**7a**) of (*R*)-(+)-**3c** with **5a** was obtained as colorless needles (4.66 g, 96% yield, mp 97−99 °C): IR 3365 and 3240 (OH), 1680 and 1625 cm^{-1}(C=O). Anal. Calcd for C$_{46}$H$_{49}$O$_6$N: C, 77.61; H, 6.94; N, 1.97. Found: C, 77.50; H, 7.02; N, 1.98.

When a solution of **3c** (1.5 g, 6.8 mmol) and **5b** (3.47 g, 6.8 mmol) in ether (10 mL) was kept at room temperature for 12 h, a 1:1 inclusion complex (**7b**) of (*R*)-(+)-**3c** with **5b** was obtained as colorless needles (3.67 g, 74% yield, mp 132−135 °C): IR 3365 and 3240 (OH), 1680 and 1625 cm^{-1} (C=O). Anal. Calcd for C$_{47}$H$_{51}$O$_6$N: C, 77.77; H, 7.08; N, 1.93. Found: C, 77.86; H, 7.08; N, 2.00.

Photoreaction of 7a and 7b in the Solid State. After irradiation of powdered **7a** (4.66 g) for 75 h, the reaction mixture was extracted with ether and chromatographed on silica gel using toluene−AcOEt (4:1) as an eluent to give (*R*)-(+)-**4c** of 87% ee as colorless needles (0.445 g ,31% yield, mp 143−145 °C, [α]$_D$ +88° (*c* 4.5 MeOH)).

After irradiation of powdered **7b** (3.67 g) for 53 h, the reaction mixture was extracted with ether and chromato-

graphed by the same method as described above to give (+)-**4c** of 85% ee as colorless needles (0.41 g, 37% yield, mp 141–144 °C, $[\alpha]_D$ +88° (*c* 4.0, MeOH)).

Conversion of (S)-(−)-3c to (R)-(+)-3c by Mixing with 12 and the Formation of 7b Which Upon Irradiation Gives (+)-4c. A mixture of (−)-**3c** (0.11 g, 0.5 mmol) and **12** (0.26 g, 0.25 mmol) was ground for 4 h by using mortar and pestle to give the inclusion complex of (*R*)-(+)-**3c** with **5b** (**7b**). **7b** was irradiated for 5 h and chromatographed on silica gel using toluene−AcOEt (4:1) as eluent to give (*R*)-(+)-**4c** of 76% ee (38% yield).

Crystal data for 3c: $C_{13}H_{17}NO_2$, M = 219.28, space group $P2_1P2_1P2_1$, a = 7.5905(5) Å, b = 12.3453(5) Å, c = 13.3201(7) Å, Z = 4, D_c = 1.167 g cm^{-3}. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Cu Kα radiation and corrected for Lorenz and polarization factors only. The structure was solved by direct methods with the use of SHELXS86[15] and refined against F^2 using SHELXL93[16] with full-matrix least-squares methods to R = 0.0327 and R_w = 0.0863 for 2341 independent, observed reflections [$I > 2\sigma$-(*I*)] with 4.88 < θ < 67.79°. All H-atoms were placed in ideal positions and refined with the riding model and fixed isotropic displacement parameters.

Crystal data for 4c: $C_{13}H_{17}NO_2$, M = 219.28, space group $P2_1$, a = 8.247(2) Å, b = 6.762(1) Å, c = 22.782(5) Å, β = 97.84-(3)°, Z = 4, D_c = 1.157 g/cm^{-3}. Data collection and the structure analysis were carried out by the same method applied to **3c**. The structure refinement was also carried out by the same method applied to **3c** with full-matrix least-squares methods to R = 0.0479 and R_w = 0.1219 for 1740 independent, observed reflections [$I > 2\sigma$(*I*)] with 3.92 < θ < 58.26°. All H-atoms were placed in ideal positions and refined with the riding model and fixed isotropic displacement parameters.

Crystal data for 7b: $C_{47}H_{51}NO_6$, M = 725.92, space group $P2_1$, a = 10.279(5) Å, b = 9.586(6) Å, c = 20.754(4) Å, β = 95.69-(3)°, Z = 2, D_c = 1.185 g cm^{-3}. Data were collected on a Rigaku AFC7R automatic four-circle X-ray diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.710 69 Å) radiation and a rotating anode. Absorption correction was applied. No degradation of the crystal by X-ray was ascertained by repeated monitoring of the three representative reflections every 150 reflections. The structure was solved by direct methods (MITHRIL84[17]) and refined with full-matrix least-squares methods to R = 0.050 and R_w = 0.071 for 2575 independent observed reflections [$I > 3.00\sigma(I)$] of 3828 unique reflections with 2θ < 50.0°. GOF = 1.26. All the calculations were carried out on teXsan crystallographic software package, Molecular Structure Corporation.[18]

Supporting Information Available: Tables of data and details of crystal structure determinations, bond lengths and angles, and anisotropic displacement parameters (42 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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