Photochemical *EZ*-Isomerization of α,β-Unsaturated Amides and Thioamides in the Solid State

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The solid-state *EZ*-isomerizability of α,β-unsaturated amides, which had low isomerizability in the solid state, was greatly improved by modifying their structure; *EZ*-isomerizability was attained by replacing the carbonyl group of the amides by a thiocarbonyl group as well as replacing the heterochiral *N*-substituent of the amides by a homochiral one. Crystallographic analyses have revealed that the isomerizability of α,β-unsaturated amides and thioamides in the solid state partially depends on their molecular conformation in crystal. In addition, it was found that the packing coefficient has a correlation with the isomerizability; a smaller value of the packing coefficient caused an increased formation of (*Z*)-isomers.

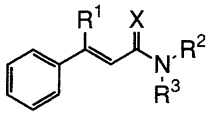
In recent decades, the crystalline environment has attracted much attention from the viewpoint of controlling the selectivity of reactions.[1] Among a number of photoreactions which have been performed in the solid state,[2] *EZ*-isomerization is still rare compared to other photoreactions,[1,3] since a drastic movement of a molecule in the crystal is required along with the reaction, which is disadvantageous for a reaction in the solid state.

As a part of our studies concerning the solid-state photoreaction of organic compounds, we recently reported that selective *EZ*-isomerization occurred for ammonium α,β-unsaturated carboxylates in the solid state upon UV-irradiation, and that the isomerizability could be controlled by a characteristic hydrogen-bond network formed in the salt crystals.[4] During a continuous study of the solid state photoreaction of α,β-unsaturated carboxylic acid derivatives, we found that *EZ*-isomerization also proceeded in the solid state even in the cases of amides and thioamides, derived from α,β-unsaturated carboxylic acids, with a complete or partial depression of another photoreaction, such as deconjugation reaction. Since the characteristics of *EZ*-isomerization in the solid state have not yet been thoroughly investigated, we studied this phenomenon in detail.

Here, we report on the solid-state photoreaction of α,β-unsaturated amides and thioamides, and discuss the relationship between the reaction behavior and the crystal structure.

Results and Discussion

Photoreaction of α,β-Unsaturated Amides and Thioamides in the Solid State. The substrates for the photoreaction in the solid state, α,β-unsaturated amides **1a—e** (see Fig. 1), were synthesized by reactions of the corresponding acid chlorides with amines. Among them, **1c** could not be a substrate, since it did not crystallize at room temperature. When α,β-unsaturated amides **1a—e** (except for **1c**) were irradiated in the solid state with a 500-W super-high-pressure mercury lamp at room temperature, only amide **1d** showed photoreactivity; the other amides were quite photostable (Table 1, Entries 1, 2, 4, and 10).[5] Photoirradiation of **1d** gave (*Z*)-isomer **2d** and deconjugated product **3d** in moderate yields (Entry 8). Although the photoisomerizability of these α,β-unsaturated amides in the solid state was generally quite low, the result of the photoreaction of **1d** prompted us to continue this study with the expectation that the *EZ*-isomerization of α,β-unsaturated compounds in the solid state might occur under appropriate conditions, which would be achieved upon a slight modification of the structure of **1a—e**.

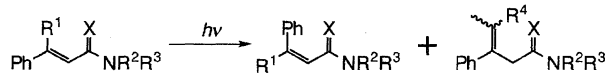


	R^1	R^2	R^3	X
1a	Et	Ph	Ph	O
1b	Et	Ph	Me	O
1c	Et	$-(CH_2)_5-$		O
1d	Et	–CHMePh-(*R*, *S*)	H	O
1e	Pr^i	–CHMePh-(*R*, *S*)	H	O
1f	Et	Ph	Ph	S
1g	Et	Ph	Me	S
1h	Et	$-(CH_2)_5-$		S
1i	Et	–CHMePh-(*R*)	H	O
1j	Pr^i	–CHMePh-(*R*)	H	O

Fig. 1. Chemical structures of amides and thioamides used in the present study.

As the first modification of **1a—e**, we considered to change

Table 1. Photoreaction of α,β-Unsaturated Amides and Thioamides in the Solid State



1 **2** **3**: R^4 = H or Me

Entry	Compound	Irradiation time	Photoreactivity	Products ratio[a] **1**:	**2**:	**3**
1	**1a**	5 min[b]	Stable	100:	0:	0
2		24 h	Stable	100:	0:	0
3	**1f**	24 h	Reactive	18:	82:	0
4	**1b**	5 min[b]	Stable	100:	0:	0
5	**1g**	95 h	Reactive	77:	23:	0
6	**1c**[c]	—	—		—	
7	**1h**	24 h	Reactive	48:	52:	0
8	**1d**	24 h	Reactive	36:	42:	22
9	**1i**	24 h	Reactive	24:	70:	6
10	**1e**	5 min[b]	Stable	100:	0:	0
11	**1j**	72 h	Reactive	60:	40:	0

a) Determined by a ^{1}H NMR analysis of the irradiated sample. b) Irradiation was performed on a sample dispersed in a KBr pellet. c) Not crystallized.

the carbonyl group of these amides to a thiocarbonyl group on the basis of the facts that a thiocarbonyl group is known to show a lower activity for hydrogen abstraction than does a carbonyl group,[6] also, the thioamides crystallize more easily than do amides.

We first tried to synthesize the corresponding thioamides from **1a**—**e** by using Lawesson's reagent.[7] In the transformation of **1d** and **1e**, the resulting products were complex mixtures, and the corresponding thioamides could not be isolated. In contrast, from amides **1a**—**c**, the corresponding thioamides **1f**—**h** (see Fig. 1) were obtained in reasonable yields. Here, it is worth noting that thioamide **1h** solidified at room temperature, in contrast to the fact that the corresponding amide **1c** was liquid. The irradiation of thioamides **1f**—**h** was performed in the solid state using a 500-W super-high-pressure mercury lamp at room temperature in a similar manner to that of the corresponding amides. The results are summarized in Table 1 (Entries 3, 5, and 7). The photoisomerizability was largely improved by changing the carbonyl of the amides to a thiocarbonyl; each of **1f**—**h** showed high-moderate photoreactivity in the solid state to afford the corresponding (*Z*)-isomer as the sole product.

Thus, *EZ*-isomerization of α,β-unsaturated carbonyl compounds in the solid state could be achieved by utilizing α,β-unsaturated thioamides. Moreover, the high selectivity for *EZ*-isomerization was attained in the photoreaction of the thioamides in the solid state; for example, the photoreaction of thioamide **1f** in chloroform gave a very complicated mixture, whereas that in the solid state afforded the (*Z*)-isomer exclusively.

In the next stage, we planned to replace the heterochiral 1-phenylethyl moiety of **1d** and **1e** with a homochiral one on the basis of the consideration that a homochiral compound would give a different crystal structure from that of the corresponding heterochiral counterpart. Then, amides **1i** and **1j** (see Fig. 1), in which the 1-phenylethyl moiety is homochiral, were prepared using (*R*)-1-phenylethylamine as an amine component; also, the photoreaction of **1i** and **1j** in the solid state was performed in the same way as that of **1d** and **1e**. As a result, the isomerizability of **1d** was highly improved by replacing the heterochiral 1-phenylethyl moiety with a homochiral one; although the yield of the (*Z*)-isomer increased, that of the deconjugated product decreased, when homochiral **1i** was photoirradiated in the solid state (compare Entries 8 and 9 in Table 1). Moreover, in the case of **1e**, a dramatic change in the photoreactivity was observed upon replacing the heterochiral 1-phenylethyl moiety with a homochiral one. Namely, homochiral **1j** showed moderate photoreactivity in the solid state to give (*Z*)-isomer **2j** as the sole photoproduct (Table 1, Entry 11); this result is in contrast to the fact that **1e** did not show any photoreactivity in the solid state (Table 1, Entry 10).

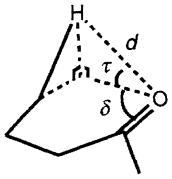
Thus, the photoisomerizability as well as selectivity of the reaction of α,β-unsaturated amide was found to be highly improved upon introducing homochirality into amides.

Selectivity and *EZ*-Isomerizability of α,β-Unsaturated Amides and Thioamides in the Solid State. As described above, the solid-state photoreaction of **1d** showed that the Norrish type-II hydrogen abstraction-deconjugation reaction occurred in competition with *EZ*-isomerization. Scheffer et al. reported on an ideal geometrical relationship between a carbonyl oxygen and a hydrogen atom for the Norrish type-II hydrogen abstraction reaction.[8] We then checked the geometrical relationship between the γ-hydrogen and the carbonyl oxygen for **1d**, **1e**, **1i**, and **1j** in the solid state on the basis of crystallographic analyses of these compounds (Fig. 2 and Table 2). As a result, it was found that each of the γ-hydrogens of **1d** and **1i** was located at a position allowed for hydrogen abstraction by the carbonyl oxygen.[8] On the basis of this molecular arrangement, the formation of the deconjugated products from **1d** and **1i** in the solid state can be reasonably interpreted.

In contrast, no deconjugated product was produced from **1e** and **1j**, even though angles τ and δ, and distance d were also within the generally allowed range for the abstraction of γ-hydrogen. This phenomenon can be explained as follows.

Table 2. Geometrical Relationship between the γ-Hydrogen and the Carbonyl Oxygen of **1d**, **1e**, **1i**, and **1j** in Crystal

Compound	τ/°[b]	δ/°[b]	d/Å[b]
1d[a]	15.5	98.9	2.15
	16.9	98.4	2.18
1i[a]	22.8	98.3	2.19
	0.8	103.3	2.17
1e	25.6	98.9	2.22
1j[a]	5.3	102.0	2.14
	20.5	97.9	2.31



a) Two molecules are included in an asymmetric unit. b) Definition of τ, δ, and d are as shown in the figure.

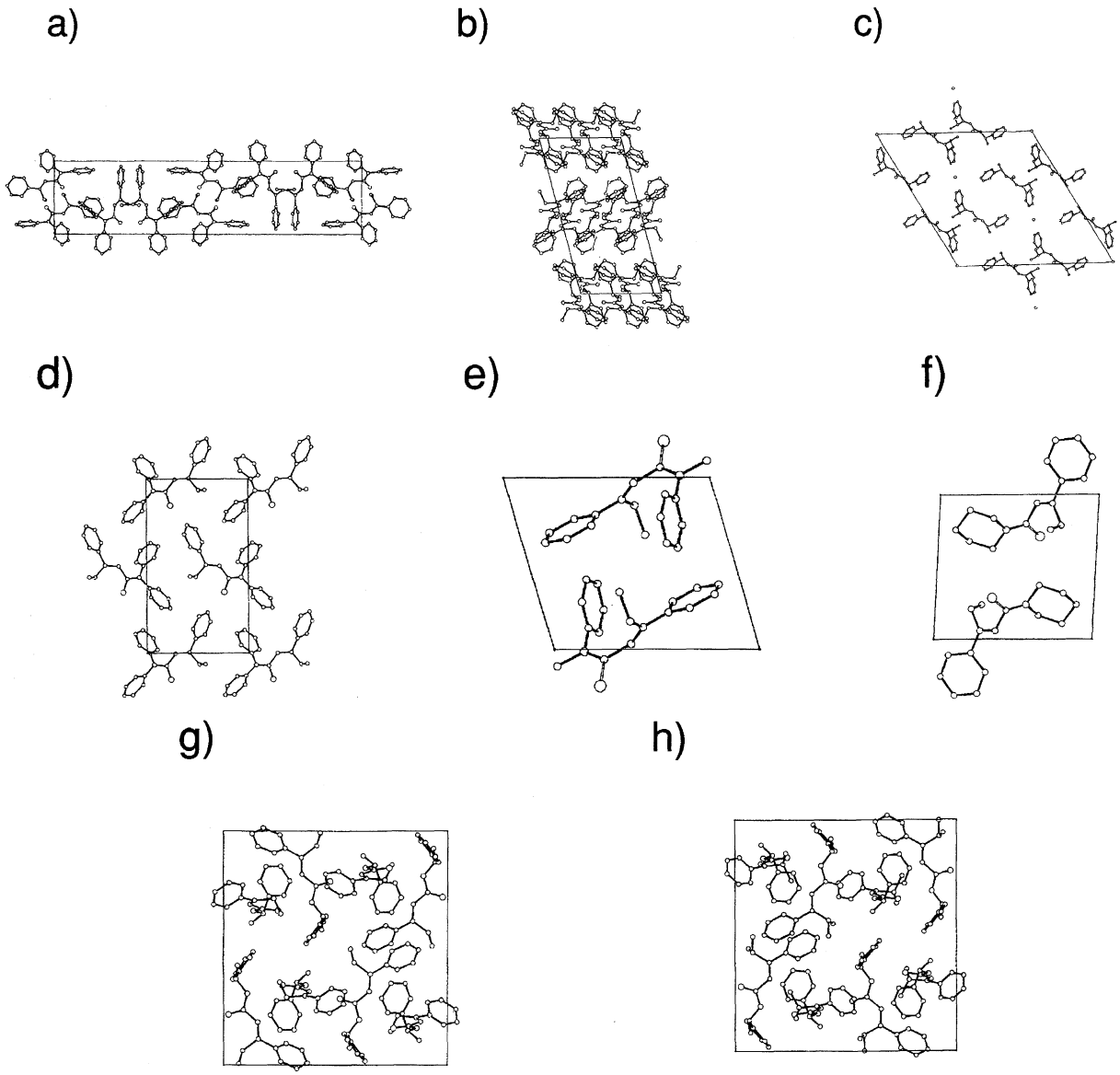


Fig. 2. Crystal structures of a) **1a**, b) **1d**, c) **1e**, d) **1f**, e) **1g**, f) **1h**, g) **1i**, and h) **1j**.

After the formation of an intermediate, a biradical or dienol, generated through hydrogen abstraction, the rate of the reverse reaction from the intermediate to the starting material is much faster than that in the process from the intermediate to the deconjugated product, which requires a large atomic movement, which is disadvantageous for a solid-state reaction. Moreover, the substituent on the γ-carbon of **1e**, which is larger than that of **1d**, would more seriously disturb the atomic movement for the deconjugation.

Thus, the selectivity of the reaction of these amides could be explained by the conformation of the amides in the solid state. We then turned our attention on the *EZ*-isomerizability of α,β-unsaturated amides and thioamides in the solid state.

Our results have shown that solid-state *EZ*-isomerization was attained by a transformation of the carbonyl group of α,β-unsaturated amides into a thiocarbonyl group or by a replacement of the heterochiral moiety of α,β-unsaturated amides by the corresponding homochiral one. Due to the effect of a thiocarbonyl group, the low ability in hydrogen abstraction as well as the crystal structure of the thioamides would affect the *EZ*-isomerizability in the solid state. The crystal structures of **1a** and **1f** showed that the most apparent difference between the amide and the thioamide in the solid state was their conformation around the isomerizing carbon–carbon double bond. For example, the dihedral angle between the carbon–carbon double bond and the thiocarbonyl plane in **1f** (43°) is larger than that in **1a** (14°) (Fig. 3). Such a large dihedral angle was also observed for **1g** (53°) as well as **1h** (53°). Since the thiocarbonyl group is twisted to the direction of the rotation, **1f**—**h** would be favorable for the *EZ*-isomerization than **1a**—**c**.

On the other hand, **1d** and **1i** (and **1e** and **1j**) have the same molecular structure and a similar molecular conformation in crystal. This means that the difference in the isomerizability cannot be explained simply based on geometry. We thus focused our attention on the vacancy in the crystals calculated

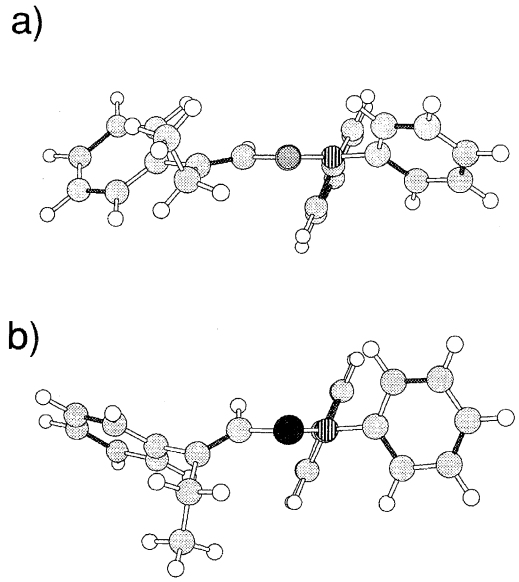


Fig. 3. Drawings of the molecular structures of a) **1a** and b) **1f** viewed from the direction of the C–O and C–S double bonds, respectively.

as packing coefficients using the program OPEC.[9] Upon comparing the packing coefficients of **1d** and **1e** with those of **1i**, or **1j**, respectively, it became clear that a smaller value of the packing coefficient leads to the formation of the corresponding (*Z*)-isomer in much higher yield (Table 3). This tendency indicates that a looser packing in the crystal is preferred for the present *EZ*-isomerization reaction in the solid state.

In our previous study concerning the *EZ*-isomerizatinon of ammonium salts of α,β-unsaturated carboxylic acids in the solid state, it was found that the isomerizability was affected by a strong hydrogen-bond network commonly formed in the salt crystals.[4] Hydrogen bonds also existed between the amide hydrogen and the amide oxygen in the crystals of **1d** and **1e**, which consequently produce a chain structure

Table 3. Packing Coefficients of Amides **1d**, **1e**, **1i**, and **1j**

Compound	$P^{a)}$	*E* : *Z* ratio
1d	0.669	46 : 54
1i	0.655	25 : 75
1e	0.665	100 : 0
1j	0.653	60 : 40

a) Packing coefficient.

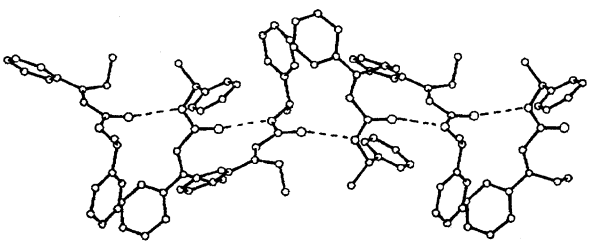


Fig. 4. Hydrogen-bond chain of crystalline **1d**. The dotted lines indicate the hydrogen bonds.

(Fig. 4). However, in the present photoreaction, the isomerizability in the solid state would be effected by the vacancy in the crystal to some extent. This result suggests that the hydrogen bonds in the amide crystal are not sufficiently strong to fix the molecule during isomerization, and that *EZ*-isomerization proceeds along with a movement of the whole amide molecule.

Experimental

General. The infrared spectra were recorded on a JASCO IR-810 spectrophotometer, and the ^{1}H NMR spectra were measured on a JEOL PMX-60SI or a JEOL GX-400 instrument with tetramethylsilane as an internal standard. The melting points were measured using a Laboratory Devices Mel-Temp and are uncorrected. Elemental analyses were performed on a Perkin–Elmer 2400 II instrument. The high-resolution mass spectra were recorded on a JEOL JMS AX-505H instrument.

Preparation of Amides and Thioamides. All of the amides were prepared from the corresponding acid halides and amines. After an acid (4.0 mmol) was added to thionyl chloride (1 ml), the mixture was stirred for 1 h at room temperature. Then, after excess thionyl chloride was removed in vacuo, dichloromethane (5 ml) was added to dissolve the crude product. To the solution was slowly added a dichloromethane (1 ml) solution of an amine (4.4 mmol) and pyridine (4.4 mmol) at 0 °C. After stirring the mixture at room temperature for 2 h, 1 mol dm^{-3} HCl (1 ml) was added. The two phases were then partitioned, and the organic layer washed with brine and dried. After removing the solvent in vacuo, the resulting mixture was separated by flash column chromatography on silica gel (eluent: hexane–ethyl acetate 10 : 1) to give pure amide, which was further purified by recrystallization from ethanol.

Thioamides **1f**—**h** were prepared by reactions of the corresponding amides with Lawesson's reagent.[7] To a dry toluene (5 ml) solution of an amide (3.0 mmol) was added Lawesson's reagent (1.5 mmol); the mixture was then refluxed for 1 h. After removing the solvent in vacuo, the resulting mixture was separated by flash column chromatography on silica gel (eluent: hexane–ethyl acetate 10 : 1). The resulting thioamides were recrystallized from a hexane–benzene (1 : 1) mixture.

(*E*)-*N*,*N*,3-Triphenyl-2-pentenamide (1a): Colorless crystals; mp 91—92 °C; IR (KBr) 1660, 1610, 1495, 1250, 870, 760, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.08 (t, J = 7 Hz, 3H), 3.11 (q, J = 7 Hz, 2H), 5.98 (s, 1H), 7.28, 7.37 (s, s, 15H). Found: C, 84.28; H, 6.43; N, 4.15%. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.27%.

(*E*)-*N*-Methyl-*N*,3-diphenyl-2-pentenamide (1b): Colorless crystals; mp 68—69 °C; IR (KBr) 1640, 1495, 1260, 860, 760, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.05 (t, J = 7.6 Hz, 3H), 3.03 (q, J = 7.6 Hz, 2H), 3.38 (s, 3H), 5.81 (s, 1H), 7.16—7.41 (m, 10H). Found: C, 81.53; H, 7.26; N, 5.16%. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.21; N, 5.28%.

1-[(*E*)-3-Phenyl-2-pentenoyl]piperidine (1c): Colorless liquid; IR 2940, 1620, 1430, 1215, 850, 760, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.03 (t, J = 8 Hz, 3H), 1.33—1.96 (m, broad, 6H), 2.75 (q, J = 8 Hz, 2H), 3.28—3.85 (m, broad, 4H), 6.22 (s, 1H), 7.31—7.69 (m, 5H). Found: C, 78.87; H, 8.54; N, 5.81%. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76%.

(*RS*,*E*)- 3- Phenyl- *N*- (1- phenylethyl)- 2- pentenamide (1d): Colorless crystals; mp 106—109 °C; IR (KBr) 3310, 1640, 1620, 1530, 1220, 760, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.03 (t, J = 8 Hz, 3H), 1.53 (d, J = 7 Hz, 3H), 3.05—3.13 (m, 2H), 5.21 (q, J = 7 Hz, 1H), 5.84 (s, 1H), 5.86 (s, 1H), 7.22—7.39 (m, 10H). Found: C,

81.93; H, 7.64; N, 5.09%. Calcd for $C_{19}H_{21}NO$: C 81.68; H, 7.57; N, 5.01%.

(*RS*,*E*)-4-Methyl-3-phenyl-*N*-(1-phenylethyl)-2-pentenamide (1e): Colorless crystals; mp 99—100 °C; IR (KBr) 1630, 1550, 1235, 760, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.04 (d, J = 6.9 Hz, 3H), 1.07 (d, J = 6.9 Hz, 3H), 1.52 (d, J = 6.9 Hz, 3H), 4.14 (m, 1H), 5.19 (m, 1H), 5.56 (s, 1H), 5.80 (d, J = 7 Hz, 1H), 7.14—7.35 (m, 10H). Found: C, 81.69; H, 8.08; N, 5.00%. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.78%.

(*E*)-*N*,*N*,3-Triphenyl-2-pentenethioamide (1f): Yellow crystals; mp 116—118 °C; IR (KBr) 1630, 1595, 1490, 1370, 1330, 1200, 1070, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.92 (t, J = 8 Hz, 3H), 2.89 (q, J = 8 Hz, 2H), 6.24 (s, 1H), 7.07—7.11 (m, 3H), 7.21—7.43 (m, 12H). Found: C, 80.17; H, 6.17; N, 4.06%. Calcd for $C_{23}H_{21}NS$: C, 80.42; H, 6.16; N, 4.07%.

(*E*)-*N*-Methyl-*N*,3-diphenyl-2-pentenethioamide (1g): Yellow crystals; mp 100—102 °C; IR (KBr) 1645, 1610, 1495, 1380, 1260, 1120, 870, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.87 (t, J = 7.3 Hz, 3H), 2.76 (q, J = 7.3 Hz, 2H), 3.82 (s, 3H), 5.99 (s, 1H), 6.95—7.41 (m, 10H). Found: C, 76.53; H, 6.84; N, 4.78%. Calcd for $C_{18}H_{19}NS$: C, 76.82; H, 6.81; N, 4.98%.

1-[(*E*)-3-Phenyl-2-pentenethioyl]piperidine (1h): Yellow crystals; mp 87—89 °C; IR (KBr) 2950, 1630, 1490, 1450, 1250, 1140, 1015, 770, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.95 (t, J = 8 Hz, 3H), 1.58—1.66 (m, 2H), 1.70—1.78 (m, 4H), 2.58 (q, J = 8 Hz, 2H), 3.79 (t, J = 6 Hz, 2H), 4.28—4.32 (m, 2H), 6.29 (s, 1H), 7.26—7.46 (m, 5H). Found: C, 73.89; H, 8.22; N, 5.37%. Calcd for $C_{16}H_{21}NS$: C, 74.08; H, 8.15; N, 5.39%.

(*R*,*E*)-3-Phenyl-*N*-(1-phenylethyl)-2-pentenamide (1i): Colorless crystals; mp 96—99 °C; $[\alpha]_D^{20}$ +5.9° (c = 0.3, EtOH); IR (KBr) 3270, 1635, 1645, 1530, 1220, 750, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.03 (t, J = 8 Hz, 3H), 1.53 (d, J = 7 Hz, 3H), 3.05—3.13 (m, 2H), 5.21 (q, J = 7 Hz, 1H), 5.84 (s, 1H), 5.86 (s, 1H), 7.22—7.39 (m, 10H). Found: C, 81.78; H, 7.65; N, 4.98%. Calcd for $C_{19}H_{21}NO$: C 81.68; H, 7.57; N, 5.01%.

(*R*,*E*)-4-Methyl-3-phenyl-*N*-(1-phenylethyl)-2-pentenamide (1j): Colorless crystals; mp 97—98 °C; $[\alpha]_D^{18}$ +31.9° (c = 0.1, EtOH); IR (KBr) 1630, 1550, 1235, 760, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.04 (d, J = 6.9 Hz, 3H), 1.07 (d, J = 6.9 Hz, 3H), 1.52 (d, J = 6.9 Hz, 3H), 4.14 (m, 1H), 5.19 (m, 1H), 5.56 (s, 1H), 5.80 (d, J = 7 Hz, 1H), 7.14—7.35 (m, 10H). Found: C, 82.12; H, 7.94; N, 5.02%. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.78%.

Photoreaction of Amides and Thioamides in the Solid State. A finely powdered sample (100 mg) was placed in a quartz cell and irradiated directly with a 500-W super-high-pressure mercury lamp (Ushio USH-500D) at room temperature under an argon atmosphere. After irradiation, the ratio for the (*E*)-isomer, (*Z*)-isomer, and deconjugated product was determined by a ^1H NMR analysis of the irradiated sample. The photoproducts were separated by preparative TLC (SiO_2, hexane–ethyl acetate 5 : 1) for identification.

(*RS*,*Z*)-3-Phenyl-*N*-(1-phenylethyl)-2-pentenamide (2d): Colorless crystals; mp 90—91 °C; IR (KBr) 1650, 1610, 1550, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.04 (t, J = 6.9 Hz, 3H), 1.11 (d, J = 6.6 Hz, 3H), 2.42 (q, J = 7.0 Hz, 2H), 4.92 (m, 1H), 5.12 (br s, 1H), 5.90 (s, 1H), 6.88—6.92 (m, 2H), 7.24—7.37 (m, 8H). Found: C, 81.28; H, 7.67; N, 4.96%. HRMS: Found: M^+, m/z 279.1603. Calcd for $C_{19}H_{21}NO$: M, 279.1623.

(*RS*)-3-Phenyl-*N*-(1-phenylethyl)-3-pentenamide (3d): Colorless crystals; mp 102—103 °C; IR (KBr) 3300, 1640, 1540, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.32 (d, J = 6.9 Hz, 3H), 1.68 (d, J = 6.9 Hz, 3H), 3.30 (s, 2H), 5.02 (m, 1H), 5.78 (m, 2H), 7.04—7.36 (m, 10H). HRMS: Found: M^+, m/z 279.1606. Calcd for $C_{19}H_{21}NO$: M, 279.1623.

(*R*,*Z*)-4-Methyl-3-phenyl-*N*-(1-phenylethyl)-2-pentenamide (2j): Colorless liquid; $[\alpha]_D^{18}$ +21.9° (c = 0.1, EtOH); IR (KBr) 1650, 1600, 1310, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.04 (d, J = 6.6 Hz, 3H), 1.06 (d, J = 6.6 Hz, 3H), 1.07 (d, J = 6.6 Hz, 3H), 2.62 (m, 1H), 4.89 (m, 1H), 5.14 (br s, 1H), 5.56 (s, 1H), 6.86—6.90 (m, 2H), 7.07—7.37 (m, 8H). Found: C, 82.06; H, 8.00; N, 4.82%. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.78%.

(*Z*)-*N*,*N*,3-Triphenyl-2-pentenethioamide (2f): Yellow crystals; mp 142—145 °C; IR (KBr) 1610, 1580, 1480, 1370, 1300, 1070, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.93 (t, J = 7.3 Hz, 3H), 2.19 (q, J = 7.3 Hz, 2H), 6.40 (s, 1H), 6.48—6.54 (m, 3H), 7.03—7.51 (m, 12H). HRMS: Found: M^+, m/z 343.1404. Calcd for $C_{23}H_{21}NS$: M, 343.1395.

1-[(*Z*)-3-Phenyl-2-pentenethioyl]piperidine (2h): Yellow crystals; mp 89—90 °C; IR (KBr) 2950, 1620, 1495, 1440, 1250, 1130, 1010, 770, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.99 (t, J = 7.6 Hz, 3H), 1.62—1.63 (m, 2H), 1.70—1.76 (m, 4H), 2.58 (q, J = 7.6 Hz, 2H), 3.79 (t, J = 5.6 Hz, 2H), 4.31 (br s, 2H), 6.29 (s, 1H), 7.26—7.45 (m, 5H). Found: C, 74.14; H, 8.29; N, 5.44%. Calcd for $C_{16}H_{21}NS$: C, 74.08; H, 8.15; N, 5.39%.

Crystal-Structure Determination and Refinement. Crystals for X-ray analyses were prepared by slow evaporation of the solvent from saturated solutions in ethanol for all cases. The X-ray intensities were measured up to 2θ = 130° with graphite-monochromated Cu $K\alpha$ radiation (λ = 1.5418 Å) on a Mac Science MXC18 four-circle diffractometer by a 2θ–ω scan. All of the data were collected at room temperature. The cell dimensions were determined from about 20 reflections (50° < 2θ < 60°). The intensities and orientation of the crystals were checked by three standard reflections every 100 reflections.

The structures were solved by direct methods with SHELXS 86[10] or MULTAN 78,[11] and refined by full-matrix least-squares techniques. Some of the structures were solved and refined by applying Crystan-GM package.[12] All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were localized from a difference Fourier synthesis, except for **1e** and **1j**. The isotropic thermal parameters of the hydrogen atoms were fixed in the cases of **1e** and **1j**, and refined in the other cases. Tables of the coordinates, thermal parameters, bond lengths, and angles for all compounds have been deposited as Document No. 69014 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Crystal Data of 1a: Chemical formula $C_{23}H_{21}NO$; formula weight 327.4; space group; $P2_1/c$; Z=8; a=10.229(2), b=38.827(7), c=9.832(2) Å; β = 107.99(2)°; V=3714(1) Å^3; D_c = 1.17 g cm^{-3}; R = 0.071; R_w = 0.086 (refined with 4111 reflections).

Crystal Data of 1d: Chemical formula $C_{19}H_{21}NO$; formula weight 279.4; space group; $P2_1/c$; Z=8; a=19.148(4), b=18.753(2), c=9.606(2) Å; β = 104.46(2)°; V=3340(1) Å^3; D_c = 1.11 g cm^{-3}; R = 0.080; R_w = 0.088 (refined with 2984 reflections).

Crystal Data of 1e: Chemical formula $C_{20}H_{25}NO$; formula weight 293.4; space group; R-3; Z=18; a=26.994(2), b=26.994(2), c = 13.217(2) Å; V = 8341(2) Å^3; D_c = 1.12 g cm^{-3}; R = 0.055; R_w = 0.057 (refined with 2101 reflections).

Crystal Data of 1f: Chemical formula $C_{23}H_{21}NS$; formula weight 343.5; space group; Pn; Z = 2; a = 17.106(4), b = 9.764(2), c = 5.697(2) Å; β = 97.93(2)°; V = 942.5(4) Å^3; D_c = 1.20 g cm^{-3}; R = 0.041; R_w = 0.044 (refined with 1546 reflections).

Crystal Data of 1g: Chemical formula $C_{18}H_{19}NS$; formula weight 281.4; space group; P-1; Z = 2; a = 9.869(2), b = 10.539(2), c = 9.570(3) Å; α = 113.20(2), β = 115.69(2), γ = 68.60(2)°; V = 801.5(3) Å^3; D_c = 1.18 g cm^{-3}; R = 0.066; R_w = 0.069 (refined with

2310 reflections).

Crystal Data of 1h: Chemical formula $C_{16}H_{21}NS$; formula weight 243.3; space group; $P\text{-}1$; $Z=2$; $a=9.523(2)$, $b=10.229(2)$, $c=9.091(2)$ Å; $\alpha=96.90(2)$, $\beta=116.61(2)$, $\gamma=63.69(2)°$; $V=736.8(9)$ Å^3; $D_c=1.30$ g cm^{-3}; $R=0.076$; $R_w=0.076$ (refined with 2276 reflections).

Crystal Data of 1i: Chemical formula $C_{19}H_{21}NO$; formula weight 279.4; space group; $P2_12_12_1$; $Z=4$; $a=17.402(4)$, $b=18.153(2)$, $c=10.755(1)$ Å; $V=3397.4(9)$ Å^3; $D_c=1.09$ g cm^{-3}; $R=0.077$; $R_w=0.091$ (refined with 1906 reflections).

Crystal Data of 1j: Chemical formula $C_{20}H_{23}NO$; formula weight 293.4; space group; $P2_12_12_1$; $Z=8$; $a=17.662(3)$, $b=18.446(3)$, $c=11.070(1)$ Å; $V=3606.6(9)$ Å^3; $D_c=1.08$ g cm^{-3}; $R=0.059$; $R_w=0.058$ (refined with 2110 reflections).

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