Solid-State Photochemistry of *o*-Aroylbenzothioates: Absolute Asymmetric Phthalide Formation Involving 1,4-Aryl Migration

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Abstract: Solid-state photoreactions of *S*-(*o*-tolyl), *S*-phenyl, and *S*-(*m*-tolyl) 2-benzoylbenzothioates, which formed chiral crystals by spontaneous resolution, underwent an unprecedented intramolecular cyclization involving phenyl migration to afford optically active corresponding 3-phenyl-3-(arylthio)phthalide in good chemo- and enantioselectivities. Stereochemical assignment and substituent probe experiment of this photoreaction sequence led to a reliable conclusion that this reaction was rationalized on the basis of the aryl migration rather than the well-recognized radicalic mechanism. Furthermore, the chirality preservation in the crystals was demonstrated by means of the bisignated CD spectra, which allowed assignment of the origin of the specific CD band and the helicity of the chiral molecules.

Introduction

The asymmetric generation influenced by the chiral crystalline environment can be considered as an attractive phenomenon to obtain optically active compounds from achiral compounds.[1−3] Of particular interest in this context is the "absolute" asymmetric transformations which are influenced only by the chiral crystalline environment without any external chiral source in the starting compounds.[4−9] This situation arises when compounds crystallized by spontaneous resolution undergo reactions in the crystalline lattices yielding new stereocenters in the products. Since the solid-state reaction proceeds with least atomic or molecular movement, the X-ray crystallographic approach is very useful for investigation of the mechanistic features and reactivities.[10−14] From a mechanistic point of view, an understanding of reactions in the anisotropic constrained media is of great advantage when solution reactions perturb the reaction outcome and preclude any formulation of the mechanism. In cases where molecules in crystal lattices are allowed to react under topochemical control due to well-defined atomic arrangement, solid-state reactions proceed through the most favored pathway leading to clear results. Then, reaction courses can be rationalized from practices of the geometrical preferences.[15,16]

Since Scheffer and co-workers described the first example of an intramolecular version of the "absolute" asymmetric syntheses by means of the photochemical di-π-methane rearrangement and Norrish/Yang cyclization systems,[4] further investigations concerning intramolecular absolute asymmetric transformations have been reported.[5−9,17−23] Although there has been considerable attention attracted to this field, variations of the methodology still remain underdeveloped. Recently, we described the solid-state photoreaction of *S*-(*o*-tolyl) 2-benzoylbenzothioate (**1a**), which formed chiral crystals, led to optically active 3-phenyl-3-phenylthiophthalide (**2a**) in good enantioselectivity (Scheme 1).[20] According to the correlation that was found by X-ray crystal structure determination, between the absolute configurations of the starting compound and photoproduct, the product formation can be rationalized by an unusual pathway involving phenyl migration. To establish the validity

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(1) Addadi, L.; Lahav, M. *Origin of Optical Activity in Nature*; Walker, D. C., Ed.; Elsevier: New York, 1979; Chapter 14.

(2) Green, B. S.; Lahav, M.; Rabinovich, D. *Acc. Chem. Res.* **1979**, *12*, 191−197.

(3) Sakamoto, M. *Chem. Eur. J.* **1997**, *3*, 684−689.

(4) Evans, S. V.; Garcia-Garibay, M.; Omkaram, N.; Scheffer, J. R.; Trotter, J.; Wireko, F. *J. Am. Chem. Soc.* **1986**, *108*, 5648−5650.

(5) Gudmundsdottir, A. D.; Lewis, T. J.; Randall, L. H.; Scheffer, J. R.; Rettig, S. J.; Trotter, J.; Wu, C.-H. *J. Am. Chem. Soc.* **1996**, *118*, 6167−6184.

(6) Toda, F.; Yagi, M.; Soda, S. *J. Chem. Soc., Chem. Commun.* **1987**, 1413−1414.

(7) Sekine, A.; Hori, K.; Ohashi, Y.; Yagi, M.; Toda, F. *J. Am. Chem. Soc.* **1989**, *111*, 697−699.

(8) Toda, F.; Miyamoto, H.; Koshima, H.; Urbanczyk-Lipkowska, Z. *J. Org. Chem.* **1997**, *62*, 9261−9266.

(9) Roughton, A. L.; Muneer, M.; Demuth, M. *J. Am. Chem. Soc.* **1993**, *115*, 2085−2087.

(10) Scheffer, J. R.; Garcia-Garibay, M.; Nalamasu, O. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York and Basel, 1987; Vol. 8, pp 249−338.

(11) Gamlin, J. N.; Jones, R.; Leibovitch, M.; Patrick, B.; Scheffer, J. R.; Trotter, J. *Acc. Chem. Res.* **1996**, *29*, 203−209.

(12) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433−481.

(13) Venkatesan, K.; Ramamurthy, V. *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH: New York, 1991; pp 133−184.

(14) Ito, Y. *Synthesis* **1998**, 1−32.

(15) (a) Zimmerman, H. E.; Zuraw, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 2358−2361. (b) Zimmerman, H. E.; Zuraw, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 7974−7989. (c) Zimmerman, H. E.; Zhu, Z. *J. Am. Chem. Soc.* **1995**, *117*, 5245−5262.

(16) Choi, T.; Peterfy, K.; Khan, S. I.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 12477−12478.

(17) Sakamoto, M.; Hokari, N.; Takahashi, M.; Fujita, T.; Watanabe, S.; Iida, I.; Nishio, T. *J. Am. Chem. Soc.* **1993,** *115*, 818.

(18) Sakamoto, M.; Takahashi, M.; Fujita, T.; Watanabe, S.; Iida, I.; Nishio, T. *J. Org. Chem.* **1995**, *60*, 3476−3477.

(19) Sakamoto, M.; Takahashi, M.; Shimizu, M.; Fujita, T.; Nishio, T.; Iida, I.; Yamaguchi, K.; Watanabe, S. *J. Org. Chem.* **1995,** *60*, 7088−7089.

(20) Sakamoto, M.; Takahashi, M.; Moriizumi, S.; Yamaguchi, K.; Fujita, T.; Watanabe, S. *J. Am. Chem. Soc.* **1996**, *118*, 8138−8139.

(21) Sakamoto, M.; Takahashi, M.; Kamiya, K.; Yamaguchi, K.; Fujita, T.; Watanabe, S. *Am. Chem. Soc.* **1996**, *118*, 10664−10665.

(22) Takahashi, M.; Fujita, T.; Watanabe, S.; Nishio, T.; Iida, I.; Aoyama, H. *J. Org. Chem.* **1997**, *62*, 6298−6308.

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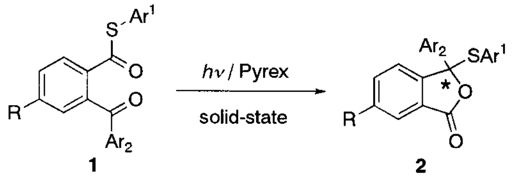
Scheme 1



a) R = H, Ar^1 = (*o*-tol), Ar^2 = Ph
b) R = H, Ar^1 = Ph, Ar^2 = Ph
c) R = H, Ar^1 = (*m*-tol), Ar^2 = Ph
d) R = H, Ar^1 = (*p*-tol), Ar^2 = Ph
e) R = Me, Ar^1 = Ph, Ar^2 = Ph
f) R = H, Ar^1 = Ph, Ar^2 = (*p*-tol)
g) R = H, Ar^1 = Ph, Ar^2 = (*p*-ClPh)

and generality of this reaction, we have investigated the solid-state photoreactions of various thioester analogues. In the present publication, complete details on the mechanistic events are described. Furthermore, we disclose the correlation between the absolute configuration and the nominally achiral molecules with chiral conformations shown by circular dichroism (CD) spectrum.

Results and Discussion

The starting thioesters **1** were readily prepared from commercially available thiols and the corresponding 2-aroylbenzoic acids by condensation reactions. For methyl-substituted thioester **1g**, the requisite 4-methyl-2-benzoylbenzoic acid was prepared by the Friedel–Crafts condensation of 3-methylphthalic anhydride with benzene. Recrystallization of these thioesters from chloroform–hexane solution afforded colorless prisms for all cases. All crystals were subjected to X-ray crystallographic analyses to obtain details on the molecular architecture in the crystals.

In regard to thioesters **1a**–**c**, the constituent molecules adopted orthorhombic chiral space group $P2_12_12_1$ and were frozen in helical conformations. Obviously, these molecules formed chiral crystals and spontaneous optical resolution occurred during their crystallization process, in which the molecules were associated and immobilized in chiral fashion. These interesting features were demonstrable through a measurement of the circular dichroism (CD) spectra of crystalline samples in KBr pellets.[24,25] Under such conditions conformational interconversion owing to carbon–carbon bond rotations was severely restricted and their optical activities evolving in the crystalline environment were maintained. Generally, there is equal possibility in the selection of enantiomorphic *P*- and *M*-forms of molecular configurations (Figure 1). Once crystals formed, a large amount of chiral crystals with the same optical rotatory can be selectively prepared through recrystallization by seeding the desired crystals.

Figure 2 shows CD spectra of two enantiomorphic crystals of **1a**–**c** in KBr pellets, which were independently obtained by spontaneous resolution. These crystals gave specific curves in the region between 200 and 400 nm, which were mirror images designated as (+) and (−) at the wavelength of 346 nm within inevitable error.

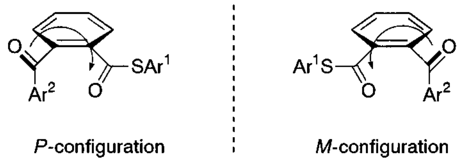


Figure 1.

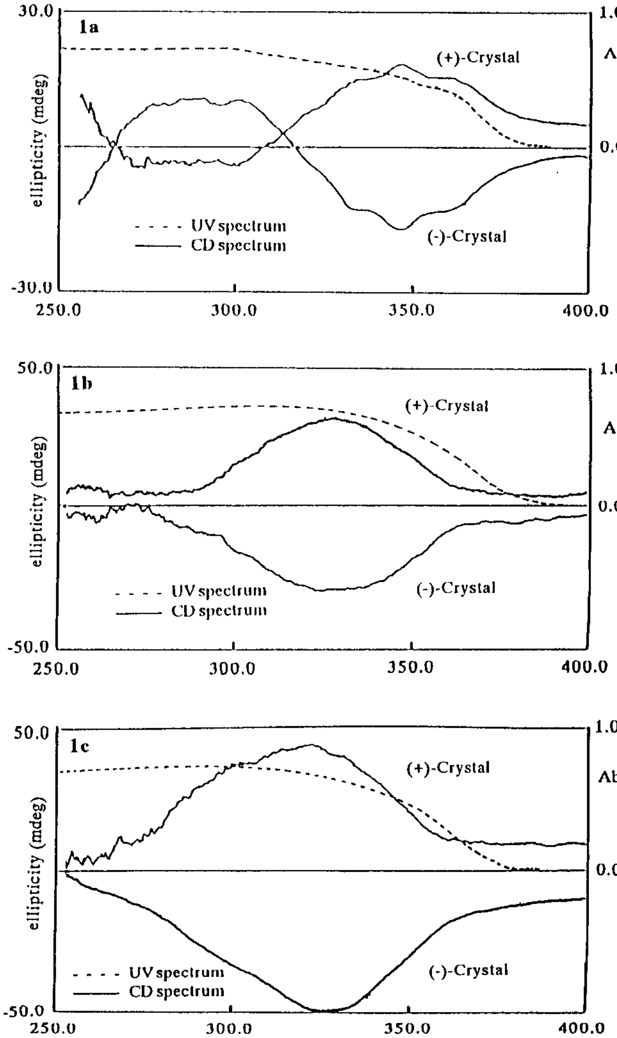


Figure 2. CD and UV spectra of enantiomeric crystals of both antipodes of **1a**–**1c** in KBr. A mixture of 10 mg of **1** and 100 mg of KBr was well ground and formed into a disk with a radius of 5 mm.

It is of great significance to correlate the absolute configurations of helical molecules frozen in the chiral crystalline environment with the sign of specific rotations. An attempt to determine the absolute configuration of (+)-**1a** giving rise to a positive Cotton effect on its CD spectrum was first successfully achieved by X-ray crystallography taking account of anomalous dispersion due to the relatively heavy sulfur atom. Consequently, the crystals (+)-**1a** were determined to contain *P*-configuration in the molecules with regard to the helix of two carbonyl groups, while its antipode was confidently assigned to possess left-handed *M*-helicity (Figure 3). Furthermore, absolute configurations of both (−)-**1b** and **1c** were determined to be *M*-configurations by X-ray crystallography. While the latter one utilized the same method as the case of (+)-**1a** for the determination, the former was established through refinement of Roger's η parameter (final value was 0.581).[26] Compatible with **1a**, both antipodes of **1b** and **1c** gave symmetrical CD absorption curves to their antipodes with almost the same intensities in all regions

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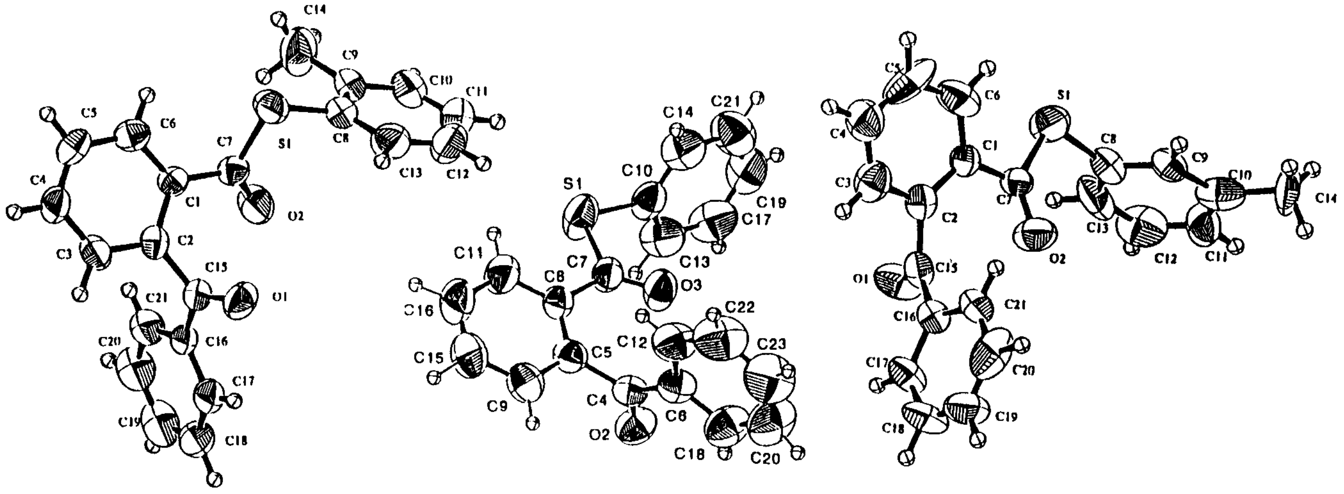
(23) Fu, T. Y.; Liu, Z.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1993**, *115*, 12202–12203.

(24) Hashizume, D.; Kogo, H.; Sekine, A.; Ohashi, Y.; Miyamoto, H.; Toda, F. *J. Chem. Soc., Perkin Trans. 2* **1996**, 61–66.

(25) For the observation of CD spectra in the crystalline state, see: Azumaya, I.; Yamaguchi, K.; Okamoto, I.; Kagechika, H.; Shudo, K. *J. Am. Chem. Soc.* **1995**, *117*, 9083–9084. Toda and co-workers also studied this topic, cited in ref 8.



Ortep drawing of (+)-1a Ortep drawing of (-)-1b Ortep drawing of (-)-1c

Figure 3. ORTEP drawings of the absolute configurations of (+)-**1a**, (−)-**1b**, and (−)-**1c**.

observed. Interestingly, a similar tendency in relationships between helicities and absolute configurations for the chiral crystals **1a**−**c** was observed, in which minus activity of the crystals was attributed to *M*-helicity while *P*-helicity was responsible for plus activity.

Figure 2 includes UV spectra of the crystals of thioesters **1a**−**c**, indicating the molecules absorbed photons sufficiently in the solid state beyond 290 nm (Pyrex filtered light).[27] Accordingly, crystals of **1d**−**g** bearing almost the same structures were expected to behave similarly on irradiation. For the practical experiment, a light source from a 500-W high-pressure mercury lamp was employed for the solid-state photoreactions of **1a**−**g**. These crystals weighing 100 mg were well ground, sandwiched between two Pyrex slides, and covered with polyethylene bags to prevent the sample from being flattened by cooling solvents during irradiation. For instance, 6 h of irradiation of powdered (+)-**1a** at 0 °C led to production of 3-phenyl-3-(*o*-tolylthio)-phthalide (**2a**) as a major product (65% yield after purification by silica gel chromatography) with complete consumption of the starting material. This compound was well-characterized by spectroscopic methods,[28] in which a lactone carbonyl appeared at 1772 cm^{-1} in its infrared spectrum and the benzoyl carbon of **1a** at δc 189.8 ppm disappeared after the reaction. Finally, this structure was unequivocally established by X-ray crystallography as shown in Figure 4. This solid-state photoreaction establishes the ability of the crystal lattice to immobilize the molecules in chiral conformations, and the reaction seemed to proceed under the influence of the crystalline environment. As expected, the asymmetric generation in **2a** was realized by an observation of its specific rotation as +37° which corresponded to 30% ee.[29] It should be emphasized that this solid-state photoreaction proceeded heterogeneously, giving the product in low chemo- and enantioselectivities owing to undesirable reactions in incidental broken lattice sites. Figure 5 shows the reaction courses in chemical yields and enantiomeric excesses of **2a** as a function of reaction proceeding at 0 °C. While the chemoselectivity decreased proportionately with the extent of irradiation, the enantioselectivity fell off seriously at earlier stages. These results indicate that nontopochemically controlled processes occurred in the crystal lattices at later reaction stages, which promoted nonselective reactions leading to complicated products including phthalide dimer as well as reaction in the solution phase.[27] Indeed, the change in enantioselectivity was more sensitive than that in chemoselectivity. Pronounced changes in the product profiles were recognized when the reaction was carried out at low (5%) conversion or at low temperature (−78 °C). In the former case, a good ee value (77% ee) was obtained with exclusive product formation (>95% as observed by ^{1}H NMR of the crude mixture). Under these conditions, the molecules were supposed to be still under topochemical control leading to the better stereoselective reaction in the crystals. Additionally, the reaction at −78 °C gave similar results (50% yield, 65% ee) for the same reason, where the molecules were strongly frozen in the crystal lattices. Obviously, the topochemical control was much more effective at lower temperature since 65% ee was obtained even at 50% conversion, which value corresponded to about 39% ee for 0 °C on estimation of the curve. Apart from **1a**, *S*-phenyl and *S*-(*m*-tolyl) derivatives **1b** and **1c** formed chiral crystals (space groups $P2_12_12_1$) and their solid-state photoreactions also led to optically active products with respective ee values depending on the reaction conditions (Table 1). Under well-optimized conditions, good enantiomeric excesses were eventually obtained in the products as high as 87% ee for **2b** (10% conversion at −78 °C) and 74% ee for **2c** (67% conversion at −78 °C).

These intramolecular cyclization reactions in the solid-state were also examined for other thioesters **1d**−**g**, giving the corresponding phthalides **2d**−**g**, but as racemates. The failure of generation of optical activity in the products was well in agreement with their centrosymmetric crystal systems such as $P2_1/c$ and $P\bar{1}$ (Table 2). In such crystals, both *P*- and *M*-helical molecules were regularly arranged and complementarily coupled each other. Eventually, the enantioselective transformation of each species led to the formation of a 1:1 mixture of *(R)*- and *(S)*-enantiomers (racemates) throughout the reaction stages.

In regard to the mechanism for these solid-state photoreactions, there are two possible pathways from the starting thioesters

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(26) Although the η value of (−)-**1b** is relatively small, the parameter test favored only one chirality for *M*-**1b** with the final R and R_W being 0.0448 and 0.0499 for 1609 reflections, which may guarantee the absolute helicity of the frozen molecules.

(27) Photoreactions of the thioesters in solution phase were investigated. Takahashi, M.; Fujita, T.; Watanabe, S.; Sakamoto, M. *J. Chem. Soc., Perkin Trans. 2* **1998**, 487−491.

(28) The spectroscopic data for all compounds have been reported in ref 27 and cited therein.

(29) The ee value was determined by HPLC by using a chiral cell OJ (Daicel Chemical Industries).

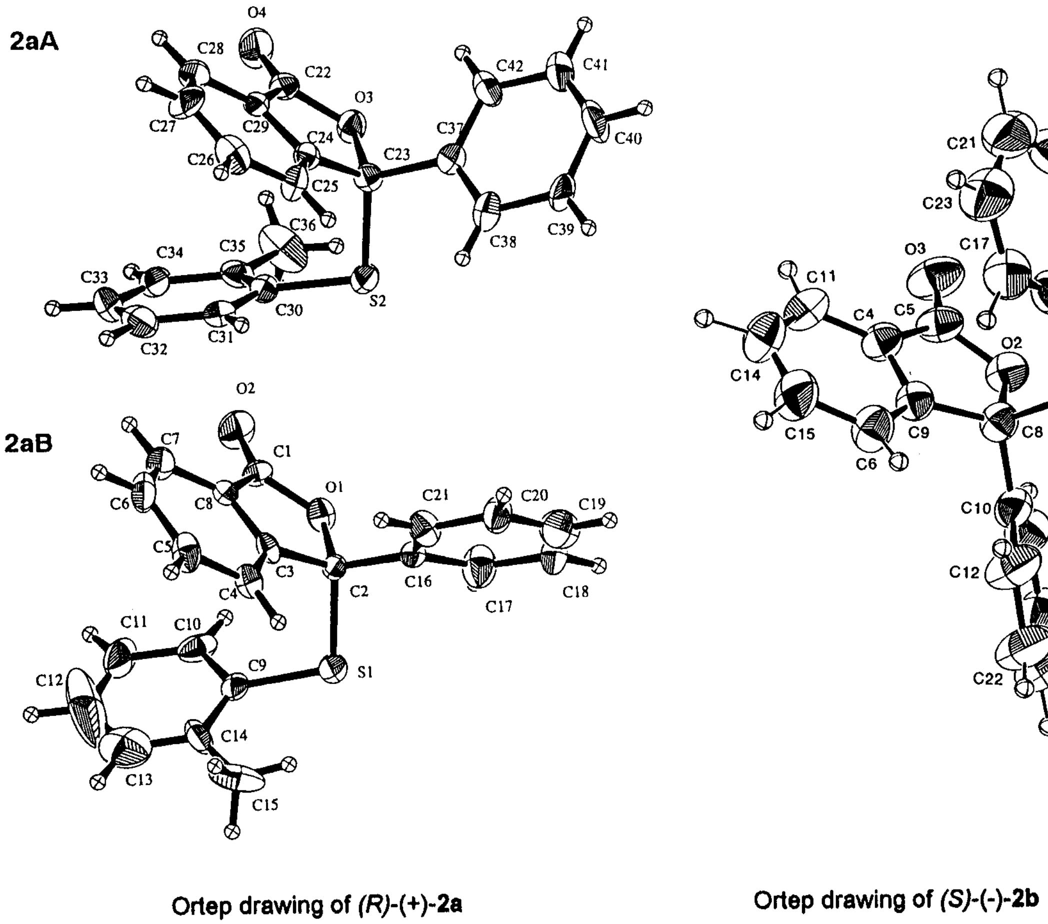


Figure 4. ORTEP drawings of the absolute configurations of *(R)*-(+)-**2a** and *(S)*-(−)-**2b**.

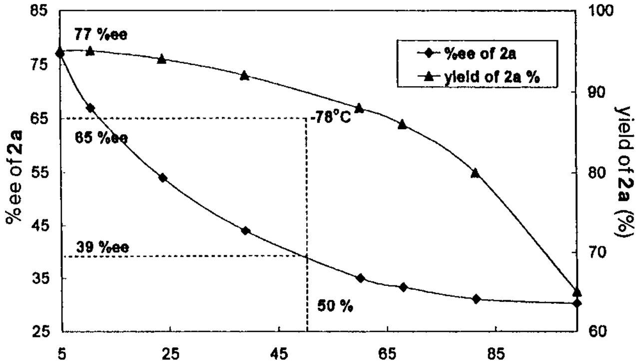


Figure 5. A plot for the conversion of **1a** vs chemical and enantiomeric yields of **2a.** The chemical yields were determined on the basis of consumed thioester **1a**.

Table 1. Solid-State Photoreactions of Thioesters **1**

thioester **1**	temp (°C)	conversion (%)	yield of **2** (%)	$[\alpha]^{20}_{D}$ of **2**$^{a-c}$
a	0	100	65	+37° (30% ee)
	0	5	>95^{d}	+94° (77% ee)
	−78	50	92	+80° (65% ee)
b	0	20	97	−37° (35% ee)
	0	10	>95^{d}	−75° (71% ee)
	−78	10	>95^{d}	−92° (87% ee)
c	0	56	96	−27° (23% ee)
	0	10	95	−83° (71% ee)
	−78	67	>95^{d}	−87° (74% ee)
d	0	100	89	0° (0% ee)
e	0	67	78	0° (0% ee)
f	0	63	91	0° (0% ee)
g	0	71	85	0° (0% ee)

[a] Measured in $CHCl_3$ at *c* 1.0. [b] Each enantiomorph could be prepared selectively in bulk by seeding methods. [c] Determined by HPLC by using chiral cell OJ (Daicel Chemical Industry). [d] The chemical yields were determined on the basis of ^{1}H NMR spectra.

to phthalides (Scheme 2). In the first model (Path A), the reaction is initiated by homolytic dissociation between C−S bonding to form a radical pair intermediate. Such a pathway is well-recognized as the excitation reaction of thioester compounds. The other model (Path B) consists of direct cyclization and subsequent phenyl migration sequences, where a zwitterionic intermediate would be involved. To solve this mechanistic problem, stereochemical correlation studies before and after the solid-state photoreactions were employed. The optically pure (+)-**2a** was obtained by optical resolution of (+)-enantiomer rich **2a** with HPLC using a chiral cell OJ, whose absolute structure was determined by X-ray analysis with the Bijvoet difference method in the correction process. Finally, the X-ray results indicated that the molecules were crystallized in triclinic chiral space group *P*1 and the unit cell included two discrete rotamers (**2a-A** and **2a-B**) owing to carbon−carbon bond rotation around the *o*-tolyl groups. Furthermore, statistic evaluation taking into account the anomalous dispersion determined the single stereocenter in (+)-**2a** to be *(R)*-configuration (Figure 4). Consequently, this reaction elucidated the stereochemical relationship from *P*-**1a** to *(R)*-**2a**.

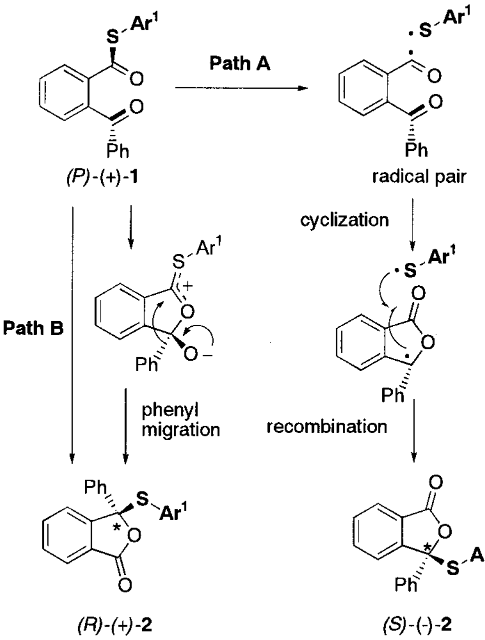
Assuming Path A was involved in the reaction, this sequence would lead to *(S)*-**2a** as a major product. This stereochemical outcome is incompatible with the aforementioned results, and this mechanistic interpretation is, therefore, ruled out. On the other hand, Path B may offer a complementary demonstration to satisfy the stereochemical relationship. The course of the

Table 2. Space Group, Optical Rotatory, and Absolute Configuration of the Starting Crystal and the Photoproduct

thioester **1**	space group	optical rotatory[a]	abs config of **1**	abs config of **2**
a	$P2_12_12_1$	(+)[b]	*P*	*R*
b	$P2_12_12_1$	(−)[b]	*M*	*S*
c	$P2_12_12_1$	(−)[b]	*M*	*S*[d]
d	$P2_1/c$	rac[c]	*PM*	*RS*
e	*P*-1	rac[c]	*PM*	*RS*
f	P-1	rac[c]	*PM*	*RS*
g	*P*-1	rac[c]	*PM*	*RS*

[a] Determined on the basis of their CD spectra at 346 nm. [b] Enantiomorphic crystals were also obtained by spontaneous crystallization. [c] Racemic crystals. [d] Predicted configuration on the basis of the Path B mechanism.

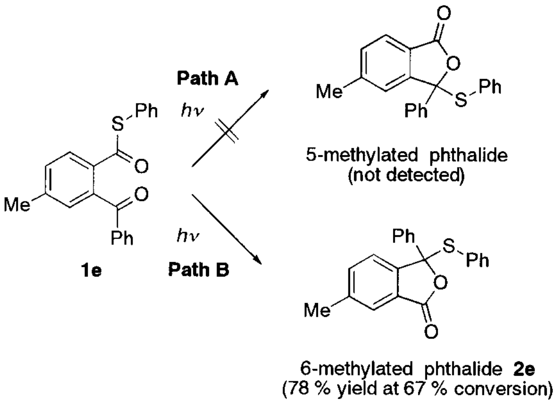
Scheme 2



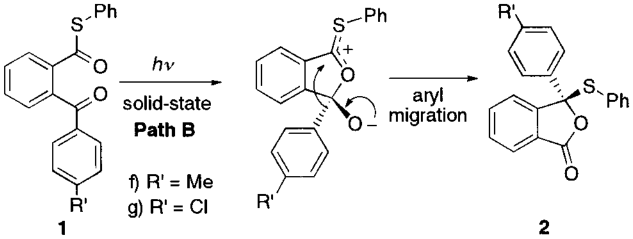
initial cyclization step may govern the absolute configuration of the final product, and the phenyl migration step proceeded with steric restrictions resulting in stereoselective formation of a single enantiomer. Thus, the enantioselective transformation from *P*-(+)-**1a** to *(R)*-**2a** can be rationalized by Path B involving a convergent sequence of nucleophilic cyclization and phenyl migration. It is noteworthy that this reaction provides new mechanistic insights into the photochemistry of thioester and aromatic compounds since both nucleophilic cyclization of the thioester group and the photoinduced 1,4-phenyl migration process have never been recognized, to the best of our knowledge.

To clarify the feasibility of stereochemical assignment during the reaction, another correlation study of the absolute configurations of the starting compound and the product was carried out for the reaction of *M*-**1b** to (−)-**2b**. The absolute structure of enantiomerically pure (−)-**2b** was determined as *(S)*-enantiomer by X-ray diffraction solving through refinement of Roger's η parameter, the final value of which was 0.865 (Figure 4). This indicated the aforementioned stereochemical relationship was applicable to this reaction system (*M*-**1b** to *(S)*-**2b**), supporting the mechanistic proposal for Path B. Unfortunately, additional assignment on the transformation of *M*-**1c** to (−)-**2c** could not be achieved since optically pure (−)-**2c** isolated by HPLC using a chiral cell gave only thin plates unsuitable for X-ray crystallographic studies. On consideration of the aforementioned discussion, the stereochemical relationship between *M*-**1c** and *(S)*-**2c** can be readily predicted.

Scheme 3



Scheme 4



An alternative approach to determine the reaction pathway was elaboration of the regiochemical correlation employing a methyl probe on the central aryl ring in the starting material. The demonstration based on the methyl probe between the starting material and final product provides straightforward proof for the determination of the pathway since the position of this substituent in the product may represent the reaction course. When the powdered sample **1e** was irradiated at 0 °C for 6 h, a single regioisomer **2e** was obtained in 78% yield (67% conversion). This photochemical event was evaluated by an observation of the ^{1}H NMR spectrum of the crude photolyzate. Remarkably, only one strong methyl signal, except for that of **1e**, evolved around the region of 2.0−2.5 ppm, with weak signals due to phthalide dimer. The demonstration is incompatible with reaction in the solution phase.[27] The characterization of the photoproduct was unequivocally established by the X-ray crystallographic analysis, which demonstrated the methyl probe was located at the 6-position of the phthalide system.[30] As is apparent from the regiochemical correlation, the reaction pathway B was indispensable for the rationalization of the product formation since Path A would lead to another regioisomer (Scheme 3). Therefore, we could draw the same conclusion as was obtained by the correlation of the absolute configurations described above for stereochemical demonstrations.

To gain further insight into the mechanistic features of the phenyl migration, solid-state photoreactions of *p*-methyl- and *p*-chlorophenylcarbonyl systems were explored (Scheme 4). The starting thioesters **1f** and **1g** were prepared from commercially available *o*-arylbenzoic acids and thiophenol by condensation with the DCC method. Along with the aforementioned cases, solid-state photolyses of crystalline samples **1f** and **1g** led to formation of cyclized products **2f** and **2g** in good yields (91 and 85%). Observation of clear methyl and aromatic signals in

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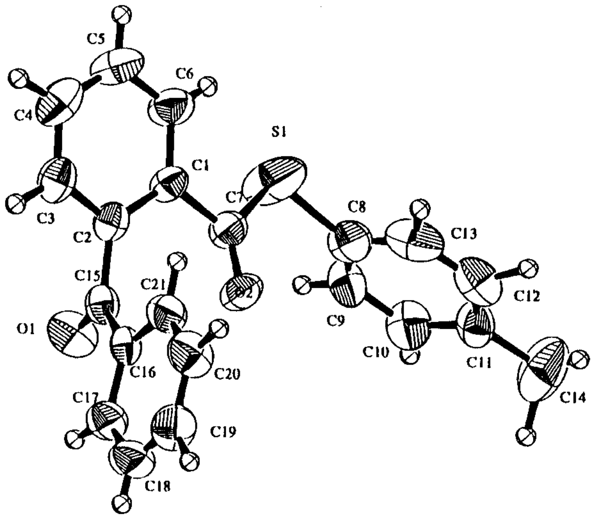
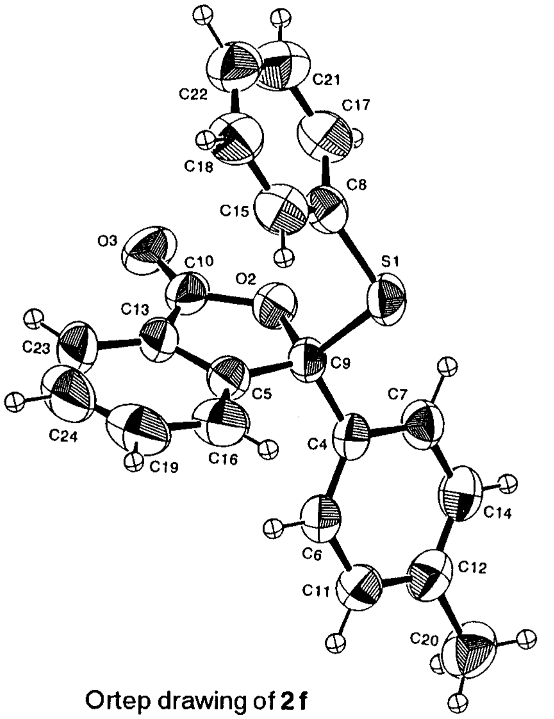
(30) The X-ray crystallographic structures of both **1e** and **2e** have been reported in ref 27, and their crystal data were cited therein.



Ortep drawing of **1 f**



Ortep drawing of **2 f**

Figure 6. ORTEP drawings of **1f** and **2f**.

the ^{1}H NMR spectra of the crude photolyzate indicated these reactions occurred with perfect regioselectivities during aryl migrations. The reaction course was also demonstrated by X-ray structural analysis of **2f**, which unequivocally ensured the aryl migration occurred in parallel fashion giving phthalide with the tolyl group at the 3-position (Figure 6).

It has been generally argued that solid-state reactions proceeded with minimum atomic or molecular movement. Therefore, the reactivities are mainly governed by atomic arrangement represented by distances and angles between reaction centers. Ultimately, geometrical assessment may offer abundant mechanistic information including crucial criteria for the feasible reactions. Twisting around the C−C bonds defined by benzoyl and thioester bending against the centered phenyl ring may be the most important factor for the formation of the helical and chiral structures. From the X-ray structural studies of the starting compounds, several trends were found in the twisting angles formed by the two functional groups, represented by α and β (Figure 7, Table 3). Remarkably, the thioester groups were inclined to exist in almost the same plane to the aryl rings (α values: 7−34°), and the benzoyl groups were orthogonally twisted with their β values of 65−93°. It is noteworthy that the sulfur atoms were located in the external spaces away from the benzoyl carbons probably due to the repulsive C═O···S interactions. With these atomic arrangements, it is difficult for straightforward radical cyclization by acyl radicals generated in Path A to occur in the crystal lattices. In such cases, C−C bond rotations around the acyl radicals should be required. However, this assumption was incompatible with the results in the improvement of enantioselectivities in lower reaction conversion and temperature since the drastic atomic movements may destroy the chiral crystalline environment, resulting in loss of enantioselective transformation. Table 3 also lists interatomic distances responsible for the photochemical events via Path B. The d_c values were much less than the sum of van der Waals radii (3.22 Å), ranging from 2.65 to 2.77 Å. Although the d_m values in this mechanism were slightly longer (3.54−3.93 Å) than the sum of van der Waals radii (3.40 Å), the subsequent aryl migration might occur since some conformational changes enhanced by initial cyclization would allow the reaction centers to be close. These atomic arrangements in the crystal lattices satisfy the reactive conformations, in which the electrophilic aroyl carbons are sufficiently exposed to the nucleophilic *n*-electrons of excited thioesters with favorable angles. Consequently, these geometrical studies also led to the same conclusion that these reactions were rationalized on the basis of the unprecedented reaction sequences consisting of the nucleophilic cyclization and subsequent aryl migration giving the cyclized products.

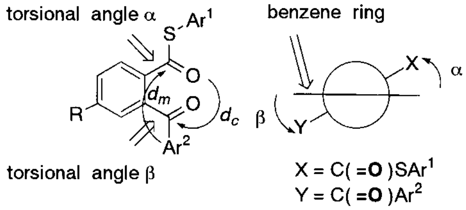


Figure 7.

Table 3. Geometrical Parameters in the Path B Mechanism[a]

thioester **1**	α (deg)	β (deg)	d_c (Å)	d_m (Å)
a	13	81	2.68	3.72
b	34	65	2.77	3.93
c	23	75	2.73	3.91
d	19	80	2.71	3.80
e	8	93	2.65	3.68
f	7	92	2.66	3.65
g	9	77	2.69	3.54
ideal			<3.22	<3.40

[a] α: torsional angle formed by the aroyl carbonyl against central aryl ring. β: tortional angle formed by the thioester carbonyl against the central aryl ring. d_c: distance between the thioester oxygen and the aroyl carbonyl carbon. d_m: distance between the carbonyl carbon of the thioester and the aryl carbon of the aroyl group.

Conclusion

Investigations of the solid-state photoreactions of *S*-aryl 2-aroylbenzothioates **1** led to the remarkable conclusion that the major process involved was an unprecedented reaction sequence, starting with intramolecular cyclization, followed by aryl migration to the photoproducts **2**. The "absolute" asymmetric generations into the achiral starting molecules were observed with good enantioselectivities, which seriously depended on the conversion and reaction temperature. The mechanistic studies based on stereochemical correlation before and after the reaction gave strong evidence for the putative reaction pathway as well as the geometrical analyses of the starting molecules in the crystal lattices. Thus, the absolute-to-absolute correlation study may offer a powerful tool for manifesting obscure reaction pathways during solid-state reactions. In conclusion, continuing elaboration of the photochemistry of such aromatic systems will provide further insights into mechanistic details of the unprecedented photochemical behavior.

Supporting Information Available: Experimental section and X-ray crystallographic data of **1b**, **1c**, **1d**, **1f**, **1g**, **2b**, and **2f** (36 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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