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Controlled Photocycloaddition of Unsaturated Carboxylates Intercalated in Hydrotalcite Clay Interlayers

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Abstract: Photochemical cycloaddition for several unsaturated carboxylates has been studied in the presence of hydrotalcite clays. Syn head-to-head cyclodimers were selectively formed in the irradiation of sodium cinnamates intercalated in the dispersed clays. On the other hand, two isomers of syn head-to-head and syn head-to-tail cyclodimers were formed for the case of (phenylethenyl)benzoates. The degree of intercalation was shown to be dependent on the structures of the carboxylates. X-ray diffraction analyses revealed that the carboxylates are intercalated as a monolayer, which suggests an alternate anti-parallel packing since a clay interlayer possesses two ionic surfaces, top and bottom. The product selectivity was shown to be controlled by the relative distances of double bonds from the ionic surfaces of the clay. The molecular aggregates of intercalated carboxylates were affected by adding photoinactive coadsorbates; the major photochemical processes shifted from photocycloadditions to cis–trans isomerizations and from excimer to monomer fluorescence emissions.

Introduction

An increasing number of studies are being reported on the photochemistry of microheterogeneous systems that accommodate photoactive species in their sterically restricted spaces.[1,2] Materials that exhibit microheterogeneous environments include inorganic substances such as silica or alumina,[3] zeolites,[4] and clay minerals[5] as well as organic aggregates such as micelles,[6–8] vesicles,[9,10] and mono- and multilayers.[11] Clays, ubiquitous lamellar aluminosilicates, can intercalate various molecular species, charged or neutral. Intercalation is based on electrostatic interactions between the ionic sites of the interlayer surfaces and ionic guest molecules.[12] For example, Lagaly has reported the formation of a bilayer film of surfactant alkylammonium ions on the interlayer surfaces of montmorillonite.[13]

In previous papers, we have reported on the stereoselective photocyclodimerization of stilbazolium ions (Stz$^+$) intercalated in saponite clay minerals.[14] The stereoselective photocyclodimerization to give the syn head-to-tail dimer was explained in terms of an intercalated monolayer of Stz$^+$ ions in alternately oriented anti-parallel fashion.[14a] Another interesting point was the fact that the mobility of guest molecules increased with increasing degree of intercalation, suggesting the catalytic utilization of the clay.[14c]

On the other hand, the photochemical reaction of intercalated anionic substrates have scarcely been studied. Hydrotalcites are anion-exchange clays possessing layered sheets composed of edge-shaped $Mg(OH)_2$ octahedral units, about one-third of which are substituted with Al^{3+} ions. Anions such as Cl^-, CO_3^{2-}, and OH^- are incorporated in the interlayers and are easily exchanged by other anions. Herein, we report a controlled photocycloaddition of olefinic carboxylates intercalated in hydrotalcite clays, the intercalation state being elucidated by excimer fluorescence and X-ray diffraction analyses.

Results and Discussion

Hydrotalcite clays employed in the present work were Kyowaad 2200 and Alcamac, manufactured by Kyowa Chemicals Ltd. The former mineral is an anhydrous metal oxide, $(Al_2O_3)(MgO)_{4.5}$, but is converted upon hydration to a hydrotalcite-like intercalate containing interlayer OH^- ions. The anion-exchange

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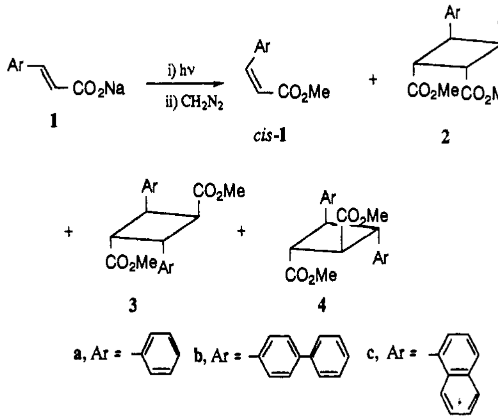
Table I. Photochemical Cyclodimerization of Unsaturated Carboxylates **1** and **5** in the Presence of Hydrotalcite Clays[a]

run no.	unsaturated carboxylate (concn, mM)	clay[b] (mM)	filter[c]	irradn time (h)	convn (%)	product yields (%)[d] cis	syn HH	syn HT	anti HH
1	**1a** (10)	18.8	q	8	92	53	46	0.7	0.4
2	**1b** (5)	7.6	p	4	98	3	97		
3	**1c** (10)	18.8	p	8	93	25	75		
4	**5a** (5)	7.6	p	4	98	6	65	27	
5	**5b** (5)	7.6	p	4	97	1	87	6	
6	**1a**[e] (5)	0	q	8	84	100			0.4
7	**1b**[e] (5)	0	p	4	93	96	4		
8	**1c**[e] (5)	0	p	4	95	100			
9	**5a**[e] (5)	0	p	4	82	66	5	25	4
10	**5a**[e] (50)	0	p	16	78	65	10	20	5
11	**5b**[e] (4)	0	p	4	86	96	0.7	4	

[a] Aqueous suspensions of sodium unsaturated carboxylates and hydrotalcite clay were irradiated with a 300-W medium-pressure Hg lamp under Ar at room temperature. [b] Kyowaad 2200 was used. [c] Symbols q and p represent quartz and Pyrex reaction vessels, respectively. [d] HH and HT represent head-to-head and head-to-tail dimers, respectively. Cis is either *cis*-**1** or *cis*-**5**. [e] Irradiation in ethanol as the corresponding methyl esters.

capacity (AEC) is 705 mequiv/100 g. Alcamac is a hydrated hydrotalcite containing chloride as the exchangeable anions in the interlayers, i.e., $[Al_2Mg_{4.5}(OH)_{13}]Cl_2{\cdot}4H_2O$, the AEC being 350 mequiv/100 g.

Photochemical Dimerization of Sodium Arylacrylate (1) in Aqueous Clay Suspensions. An aqueous suspended solution of 5 mM sodium cinnamate (**1a**) and hydrotalcite clay, Kyowaad 2200 (5.7 mM on the basis of AEC), was irradiated for 8 h with a medium-pressure 300-W Hg lamp (i.e., >250 nm) under Ar atmosphere. After the irradiation, the suspended reaction mixture was acidified with concentrated HCl to decompose the clay and extracted with dichloromethane. The reaction mixture was methylated with diazomethane, dried over anhydrous sodium sulfate, and condensed under reduced pressure. Products were separated on a silica gel column to give five fractions including the methyl ester of **1a**. Products were identified by NMR, HPLC, and/or GLC in comparison with the authentic samples (see Experimental Section). The predominant form was the syn head-to-head dimer **2a**, although trace amounts of other isomeric dimers (**3a** and **4a**) were also detected (run 1 in Table I). A control experiment in the absence of clay (run 6) showed that the clay changed the reaction course dramatically from cis–trans isomerization to the selective cyclodimerization.



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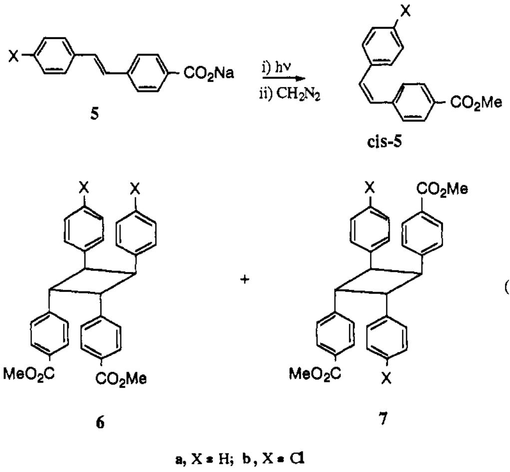
Sodium *p*-phenylcinnamate (**1b**) and sodium 1-naphthylacrylate (**1c**) were irradiated in the presence of hydrotalcite clay similarly but through a Pyrex filter (i.e., >290 nm). As shown in runs 2 and 3, the resulting dimers were solely the corresponding syn head-to-head dimers **2** not contaminated with other isomers (**3** or **4**). Table I shows that the methyl esters of **1b** and **1c** in the absence of clay in ethanol underwent photochemical cis–trans isomerization (runs 7 and 8).

Photochemical Dimerization of Sodium Stilbenecarboxylate (5) in Aqueous Clay Suspensions. UV irradiation of sodium *p*-(2-phenylethenyl)benzoate (**5a**) in the presence of suspended hydrotalcite clay resulted in the predominant formation of two cyclodimers in the ratio of 2.4:1 as determined by HPLC. Silica gel chromatography of the mixture, after the methylation with diazomethane using dichloromethane as an eluent, isolated two cyclodimers (A and B of retention times of 18.1 and 11.8 min by HPLC). Their molecular ion peaks at *m/e* 476 in the mass spectrum indicated that they are isomeric cyclodimers of **5a**. In their NMR spectra the methine protons appeared at 4.53 ppm as an octet and a singlet for A and B, respectively, which implies that they are syn dimers. This is based on the reported stereochemical assignment of stilbene dimers in which a proton cis to adjacent phenyl group gives resonance at a higher field (i.e., 3.63 ppm) than when it is trans (4.40 ppm).[15,16] The characterization was further accomplished by converting the two syn dimers A and B to more thermally stable anti isomers under the reported epimerization conditions (i.e., excess KOH and 350 °C).[17] The mass spectrum of the epimer from A showed a fragment ion of *p,p'*-(dimethoxycarbonyl)stilbene at *m/e* 296 in addition to the starting monomer fragment ion at *m/e* 238, whereas that from B showed only the latter one (*m/e* 238); this indicates that the former is a head-to-head dimer and the latter is a head-to-tail one. In addition, the NMR spectra of dimers A and B showed, on epimerization, an upfield shift of methine protons from 4.53 to 3.75 ppm and a downfield shift of aromatic ortho protons from 7.80 to 8.00 ppm, both of which are due to the more effective shielding effect by adjacent aromatic rings of anti isomers.[15] Thus, dimers A and B could be assigned as the syn head-to-head (**6a**) and syn head-to-tail dimers (**7a**), respectively.



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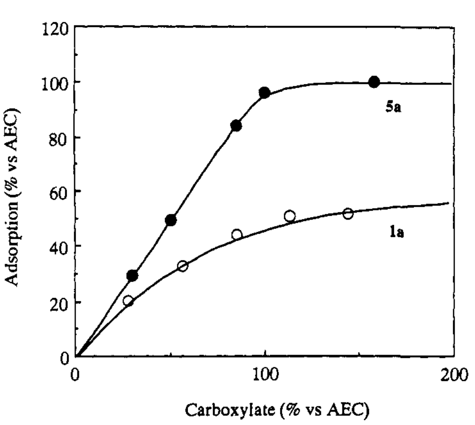

Figure 1. Uptake curves for intercalation of unsaturated carboxylates **1a** and **5a** in hydrotalcite clay suspended in water at room temperature. Concentrations: (○) [**1a**] = 10.0 mM, [clay] = 7.0–35.0 mM; (●) [**5a**] = 5.0 mM, [clay] = 1.4–7.5 mM.

The photodimerization of sodium *p*-[2-(*p'*-chlorophenyl)-ethenyl]benzoate (**5b**) in the presence of clay afforded two cyclodimers, which were analyzed similarly (see Experimental Section for details). The resulting ratio of syn head-to-head (**6b**) and syn head-to-tail (**7b**) was 14.5:1, much higher than in the case of **5a**. All of the above results indicate the dramatic effect of the anion-exchange clay in controlling the photodimerization of olefinic carboxylate anions. It is also apparent that the photocycloadditions take place in the clay interlayers, since only the cis–trans isomerization of **5** was observable in the absence of clay (runs 9–11).

Intercalation of Unsaturated Carboxylates 1 and 5 on the Interlayers of Hydrotalcite Clays. Hydrotalcites are anion-exchange clays with $Mg(OH)_2$ octahedral layered sheets, about one-third of which are substituted by Al^{3+}, producing cationic charges. Appropriate exchangeable anions, e.g., Cl^-, CO_3^{2-}, and OH^-, equivalent to the number of aluminum atoms are introduced in the interlayers in order to compensate for the excess cationic charges. Kyowaad 2200 employed here is an anhydrous metal oxide $(Al_2O_3)(MgO)_{4.5}$ which, in water, is hydrated to give $[Al_2Mg_{4.5}(OH)_{13}](OH)_2$, which is similar to Alcamac, $[Al_2Mg_{4.5}(OH)_{13}]Cl_2{\cdot}4H_2O$, except that OH^- occupies the gallery rather than Cl^-. There was no essential difference in the intercalation properties of Kyowaad 2200 and Alcamac toward carboxylate anions when they were used in aqueous systems.

To an aqueous solution of 10 mM unsaturated carboxylate was added 1 equiv or a little excess amount of hydrotalcite clay powder (either Kyowaad 2200 or Alcamac), and the solution was stirred for 10 h at 60 °C. The extent of intercalation increased with increasing amounts of carboxylate, as shown in Figure 1. The intercalation of **5a** was quite effective and increased linearly with [**5a**] up to the equivalent AEC. On the other hand, the intercalation of **1a** was not so effective and increased gradually with increasing excess amount of **1a**. The degree of intercalation may be expressed by the following equilibrium equation:

$$RCO_2^-Na^+ + clay^+Cl^- \overset{K_{ad}}{\rightleftarrows} RCO_2^-clay^+ + Na^+Cl^- \quad (3)$$

where K_{ad} equals $[RCO_2^-clay^+]\cdot[Na^+Cl^-]/[RCO_2^-Na^+]\cdot[clay^+Cl^-]$.

The degree of intercalation was determined by measuring the filtrated carboxylates from 1:1 mixtures of carboxylates and hydrotalcite clay and the equilibrium constants were calculated according to eq 3. As listed in Table II, the resulting K_{ad} values for **1a** and **1c** were low, corresponding to only 35 and 39% intercalation, respectively. In contrast, K_{ad} values for **1b**, **5a**, and **5b** were relatively high, and the degree of intercalation was almost quantitative. These high levels of intercalation could be well understood since hydrophobic interactions between guest molecules are known to be important in the intercalation on interlayer surfaces of clays. The rather poor adsorption of naphthylacrylate **1c** seems to indicate that nonlinear bulky molecules are not appropriate for the intercalation. It is also interesting to note that the intercalation of head-to-head dimer **2a** is much effective than that of head-to-tail dimer **3a**.

Table II. Equilibrium Constants (K_{ad}) for the Intercalation of Unsaturated Carboxylates **1** and **5** and Related Dimers on Suspended Hydrotalcite Clays in Water[a]

carboxylates	equilibrium constant (K_{ad})[a]	degree of intercalation (%)[b]
1a	0.3	35
1b	280	94
1c	0.4	39
5a	2100	98
5b	56	88
2a	12	74
3a	0.034	15

[a] Equilibrium constants were calculated according to eq 3. [b] Degrees of intercalation were estimated from the amount of carboxylates in the filtrates from 1:1 mixtures of unsaturated carboxylates and clay in water at room temperature.

Table III. Correlation between Gallery Height of Intercalated Clays and the Resulting Cyclodimer Selectivity

intercalated carboxylate	molecular length (Å)[a]	gallery height (Å)[b]	distance between two double bonds (Å)[c]		major products[d]
			*d*HH	*d*HT	
1a	9.10	13.6	0	7.58	syn HH
1b	13.1	17.5	0	11.5	syn HH
5a	13.2	17.5	0	2.78	syn HH + syn HT
5b	14.8	18.5	0	3.68	syn HH + syn HT

[a] Molecular lengths of carboxylates were estimated from an AM1 molecular orbital calculations. [b] Gallery heights were calculated by subtracting the $Mg(OH)_2$ sheet thickness (4.77 Å) from the interlayer distances obtained from X-ray diffraction analysis. [c] Differences between two double bonds in distances from the interlayer surface. The *d*HT values were calculated from the gallery heights and the distances of double bonds from the carboxylate groups (see Figure 2). The *d*HH values for HH packing are 0 as listed. [d] Stereochemistries of the major cyclodimers formed in the photocycloaddition of intercalated olefinic carboxylates.

Molecular Packing. Modes of intercalation could be deduced from the X-ray diffraction analysis of intercalated clay powders. Thus, intercalated clays were filtered and dried in vacuo at room temperature, and the dried clay powders were analyzed by X-ray diffraction spectroscopy. The gallery heights were calculated by subtracting the $Mg(OH)_2$ sheet thickness of 4.77 Å from the 003 basal spacings. The gallery heights for the intercalated Cl^- was 2.9 Å. As shown in the third column in Table III, the intercalation of carboxylates **1** or **5** elongated the interlayer distance up to 14–19 Å, values close to or slightly larger than the length of the guest anions. Now it is apparent that the added carboxylates are intercalated as a monolayer on the clay interlayers. This led to the conclusion that intercalated carboxylate anions are to be oriented in an anti-parallel fashion since anion-exchange sites are distributed on both sides of the clay interlayers. Such an anti-parallel packing seems to be possible since the guest carboxylate ions are anchored at anion-exchange sites distributed over the interlayer sheets every 5.2 Å.[18] The length allows enough space for the anti-parallel packing. Figure 2 illustrates simplified drawings for the anti-parallel molecular packing of **1b** and **5a**. The assumption of homogeneous scattered Al atoms in $Mg(OH)_2$ sheets has been verified by X-ray analysis.[19]

Control of Stereoselectivities in Cyclodimerization. As stated above, the unsaturated carboxylates are deduced to form an anti-

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(18) The figures of the average distance between adjacent anion sites were estimated by $3^{1/2}a$, where a is a lattice constant (3.048 Å) of a rhombic crystal system of hydrotalcite, *R*3*m*.

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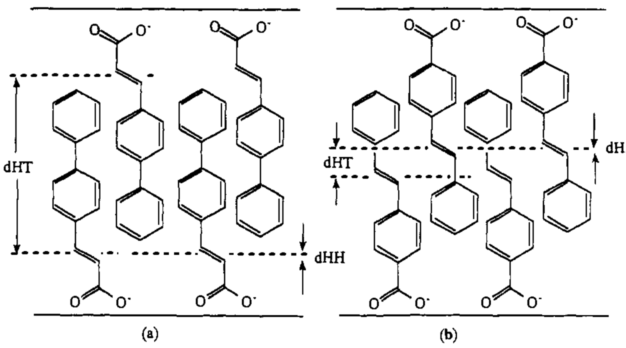

Figure 2. Simplified drawing of anti-parallel packing of (a) *p*-phenylcinnamate (**1b**) and (b) stilbenecarboxylate ions (**5a**).

parallel monolayer on the clay interlayers. Such a molecular packing, however, does not always explain straightforwardly the stereochemistry of the cyclodimers formed. While cinnamates **1a–c** yielded almost exclusively head-to-head dimers **2a–c**, (phenylethenyl)benzoates **5a** and **5b** gave significant amounts of head-to-tail dimer **7** in addition to a head-to-head isomer (**6**) (Table I). The formation of two isomers is well understood on the basis of the anti parallel packing since one olefinic molecule is surrounded both by a parallel olefin on the same surface and by an anti-parallel chain on the other surface.

The selective formation of head-to-head dimers from cinnamates may be explained by the importance of intermolecular distances of two double bonds of adjacent carboxylates. The distance of the double bonds from one surface of the interlayer could be estimated from the molecular size of carboxylates and the gallery heights. In the fourth column in Table III are listed the distances between two double bonds for the parallel and anti-parallel packing configurations. The two double bonds for the parallel (i.e., head-to-head) pairing are separated by 5.2 Å and located at the same distance from the layer surfaces (i.e., *d*HH equals 0), but those for the anti-parallel (i.e., head-to-tail) packing are quite variable, depending on the molecular structures and the gallery heights. The estimated values for the HT packing of **1a** and **1b** are over 7 Å, while the ones for **5a** and **5b** are below 4 Å. It is well established that in solid-state photochemistry a critical distance is around 4–5 Å for photochemical [2 + 2] cyclodimerizations of olefin molecules.[2] Therefore, the estimated distance of over 7 Å for the HT packing of cinnamates **1a** and **1b** is too far for effective cyclodimerization. This led to the observed selective formation of head-to-head dimers. In contrast, the dimerization of intercalated (phenylethenyl)benzoates **5** should be possible for either the head-to-head or the head-to-tail orientation, since the *d*HH and *d*HT values are below 5 Å. These analyses from product selectivities suggest that unsaturated carboxylates are intercalated in alternately oriented anti-parallel fashion and their photodimerizations are controlled by the distances of double bonds from the ionic sites of interlayers.[20]

Here it is noteworthy to compare the stereoselectivity in the present anionic clay with those of photocycloadditions of stilbazolium ions intercalated in a cationic clay (Sumecton SA).[14] In contrast to the present case, only syn head-to-tail dimers were obtained on irradiation of stilbazolium ions. No observation of the corresponding HH dimers could be tentatively attributed to the significant difference in their intercalating capability. That is, the cation-exchange capacity of Sumecton SA is only 0.1 equiv/g, which is ca. one-third of the anion-exchange capacity of Kyowaad 2200, and the mean distance for the HH pairings is deduced to be ca. 10 Å, i.e., too far to dimerize.

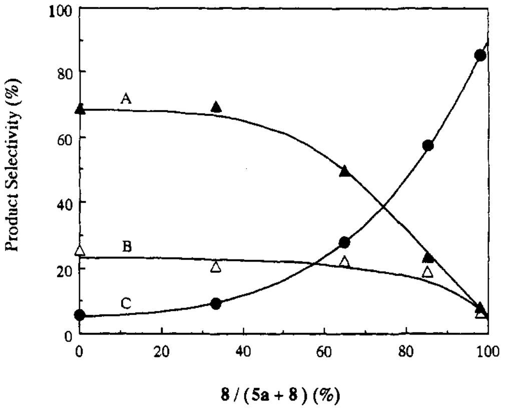

Figure 3. Effect of coadsorbate **8** on product selectivities for the irradiation of intercalated **5a** in water. Conditions: [**8**] + [**5a**], 5.0 mM, [clay] = 5.4 mM; the irradiation time was 4 h and the conversion of **5a** was >95%. A: formation of **6a** (▲). B: formation of **7a** (△). C: isomerization to *cis*-**5a** (●).

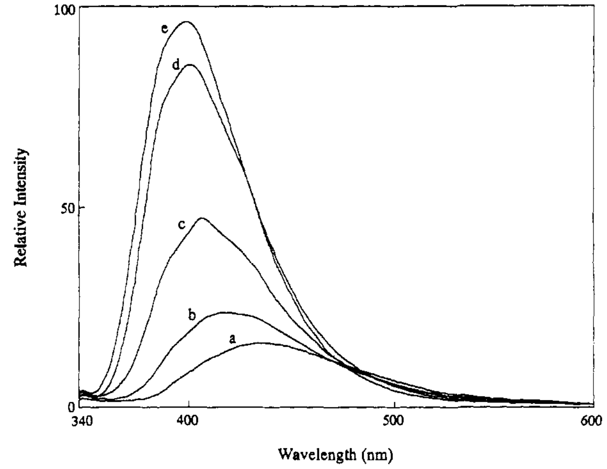

Figure 4. Diffuse reflectance fluorescence spectra of powdered clay samples on excitation at 325 nm. Intercalation ratios of **5a** and sodium caprate: (a) 100:0, (b) 50:50, (c) 25:75, (d) 10:90, (e) 5:95.

Effect of Coadsorbate Sodium *p*-Phenethylbenzoate. In order to elucidate another feature of the photodimerization of intercalated olefinic carboxylates, the effect of coadsorbates has been studied. Thus, the addition of sodium *p*-phenethylbenzoate (**8**), a photochemically inactive coadsorbate, affected significantly the product distribution in the photolysis of **5a** (Figure 3). The ratio of head-to-head (**6a**) and head-to-tail dimers (**7a**) decreased gradually from 2.4 to 1 with increasing amount of coadsorbate **8**. At the same time, the major reaction shifted from the [2 + 2] cyclodimerization to cis–trans isomerization, suggesting the increasing amount of isolated unsaturated carboxylate molecules. The 1:1 product ratio of **6a** and **7a** at high dilutions probably reflects the predominant 1:1 pairing of **5a** molecules and the equal probability of parallel and anti-parallel pairings. The product ratio of 2.4 in the absence of **8** indicates the slightly more preferable formation of head-to-head dimers when a **5a** molecule is surrounded by both neighboring parallel and anti–parallel molecules.

The dilution effect was also noticed in an excimer fluorescence study. The clay-intercalated **5a** showed excimer fluorescence at 430 nm, as shown in curve a in Figure 4. With the addition of sodium caprate as a coadsorbate, the excimer fluorescence of **5a** decreased and the monomer fluorescence at 390 nm increased gradually. These facts clearly suggest that the molecular aggregates of **5a** are diluted gradually by the addition of the coadsorbate. This is in line with the increase in cis–trans isomerization with increasing amount of coadsorbate (Figure 3).

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[20] The estimation of equilibrium intercalation geometry from product selectivities is speculative in nature because of the kinetic preference for the photoaddition. But it is our opinion that the resulting product selectivities significantly reflect the equilibrium intercalation since the photoaddition was quite efficient and the product selectivities remained unchanged even at the end of reaction.

Conclusion. The photochemical cyclodimerization of unsaturated carboxylates intercalated on hydrotalcite clay interlayers has been shown to be highly efficient and selective. X-ray diffraction studies suggested the intercalation of adsorbate monolayers and, hence, of anti-parallel fashion. The selective formation of syn head-to-head and syn head-to-tail cyclodimers suggests that the cyclodimerization is controlled by the relative distances from the interlayer surface.

Experimental Section

UV and visible spectra were recorded on a Shimadzu UV-265 spectrophotometer. Fluorescence spectra were obtained with a Hitachi 650-10 fluorescence spectrophotometer. HPLC analyses were carried out with a Jasco HPLC instrument (Model UVIDEC 100 III) detected at 250 nm using a 30-cm SIL column (Jasco) eluting with CH_2Cl_2. GLC analyses were done with a Yanagimoto G180 gas chromatograph using a 1- or 2-m column of carbowax 300M at 80–260 °C. NMR spectra were taken with a Varian Gemini-200 NMR instrument. Mass spectra were taken with a JOEL high-resolution mass spectrometer (Model D-300) employing a direct inlet system; the ionization potential was 20 eV. X-ray powder diffraction analysis was carried out with an X-ray diffractometer (Rigaku Denki) with Ni-filtered Cu $K\alpha$ radiation. The 003 basal spacings of the layers were measured by the Debye–Scherrer method. Melting points are corrected.

Materials. *p*-Phenylcinnamic acid (**1b**) was synthesized by the condensation of *p*-biphenylcarboxaldehyde with malonic acid,[21] mp 227–232 °C (lit.[21] mp 225 °C). 1-Naphthylacrylic acid was synthesized by the condensation of 1-naphthaldehyde with ethyl acetate according to a known procedure.[22] *p*-(2-Phenylethenyl)benzoic acid (**5a**) was obtained by the condensation of *p*-(hydroxycarbonyl)benzenediazonium chloride and cinnamic acid in the presence of cupric chloride,[23] mp 226–229 °C (lit.[23] mp 224–225 °C). *p*-[2-(*p*′-Chlorophenyl)ethenyl]benzoic acid (**5b**) was prepared by the reaction of (*p*-carbomethoxybenzyl)triphenylphosphonium bromide with *p*-chlorobenzaldehyde, mp 305 °C (lit.[24] mp 302–304 °C). *p*-Phenethylbenzoic acid (**8**) was synthesized by the hydrogenation of **5a** in the presence of paradium charcoal in ethanol, mp 175–177 °C (lit.[25] mp 170–172 °C).

Hydrotalcite clays, Kyowaad 2200 and Alcamac, were gifts from Kyowa Chemicals Ltd. The former is the anhydrous metal oxide, $(Al_2O_3)(MgO)_{4.5}$, and the latter is the hydration form including chloride ions in the interlayers, i.e., $[Al_2Mg_{4.5}(OH)_{13}]Cl_2 \cdot 4H_2O$. The AECs of Kyowaad 2200 and Alcamac are 705 and 350 mequiv/100 g, respectively.

Intercalation on Clay. Clay-intercalated samples were prepared by mixing 1.0–10 mM aqueous solutions of unsaturated carboxylates with slight excess amounts of the clay powder and stirring overnight at 60 °C using a Kaijo Denki 200A homogenizer. After being allowed to cool to room temperature, the suspensions were used for the following photochemical reactions. In order to prepare guest-adsorbed clay powder samples, the suspensions were filtered using a membrane filter (Toyo Roshi Co., pore size 0.45 μm), and the filtrated clays were dried in vacuo at room temperature for a few days. For the purpose of X-ray analysis, the dried samples were ground and used as powder samples.

Equilibrium Constants K_{ad} for Intercalation. After being stirred at room temperature for 1 day to attain equilibrium, the equilibrated suspensions were filtered through a membrane filter (Toyo Roshi Co., pore size 0.45 μm). The amounts of carboxylate not intercalated were estimated by the UV absorbance of the filtrate. The equilibrium constants for the intercalation on hydrotalcite interlayers were calculated according to eq 3 and listed in Table **II**.

Irradiation of Sodium Cinnamate (1a) in the Presence of Hydrotalcite Clay. To a 15-mL aqueous solution of 10 mM sodium cinnamate (**1a**) was added 40 mg of hydrotalcite clay powder, Kyowaad 2200, in a 30-mL quartz tube with a septum cap, and the mixture was stirred overnight at 60 °C. After argon gas was bubbled through for 15 min at room temperature, the suspended solution was irradiated with a 300-W medium-pressure Hg lamp for 8 h under magnetic stirring. With the addition of 15 mL of concentrated HCl, the irradiated suspension was acidified and the clays were decomposed, inducing precipitation of free carboxylic acids. The acidified solution was extracted with several 100-mL portions of CH_2Cl_2, followed by methylation with CH_2N_2 in ethyl ether, drying over anhydrous Na_2SO_4, and then condensation in vacuo to give a pale yellow oil. Products were analyzed by GLC in comparison with authentic samples prepared independently. Products, retention times (min), and yields (%) are as follows: methyl ester of *cis*-**1a**, 5.0, and 53; methyl ester of *trans*-**1a**, 6.5, and 8; syn head-to-head dimer **2a**,[26] 17.0, and 46; syn head-to-tail dimer **3a**,[27] 16.0, 0.7; anti head-to-head dimer **4a**,[17b] 17.5, and 0.4.

Irradiation of Clay-Intercalated Sodium *p*-Phenylcinnamate (1b). The intercalation of **1b** was carried out in a 30-mL Pyrex tube, and the sample was irradiated for 4 h. The products were treated as in the above case for **1a**. SiO_2 column chromatography of the reaction mixture using CH_2Cl_2 as an eluent gave a viscous semisolid: NMR (δ) carbomethoxy methyl protons (3.75, s, 6 H), cyclobutane methine protons (3.9, dd, J = 2.3, 4.2 Hz, 2 H; 4.45, dd, J = 2.3, 4.2 Hz, 2 H); aromatic protons (7.0, d, 4 H; 7.3–7.7, m, 14 H); MS; *m/e* (relative intensity) 476 (M^+, trace), 238 ($M^+/2$, 100). Product analysis was done on a HPLC using a Jasco SIL column with CH_2Cl_2 as an eluent at a flow rate of 1 mL/min. Product, retention times (min), and yield (%): methyl ester of *cis*-**1b**, 5.5, and 3; methyl ester of *trans*-**1b**, 8.5, and 2; syn head-to-head dimer **2b**, 20.0, and 96.

Irradiation of Clay-Intercalated Sodium 1-Naphthylacrylate (1c). The sample suspension was prepared similarly and irradiated in a 30-mL Pyrex reaction vessel for 8 h. The reaction mixture was treated similar to that of **1a**. GLC analysis of the resulting mixture was done in comparison with authentic samples prepared independently. Product, retention times (min), and yield (%): methyl ester of *cis*-**1c**, 9, and 25; methyl ester of *trans*-**1c**, 10, and 7; syn head-to-head dimer **3c**,[26] 25, and 75.

Irradiation of Intercalated Sodium *p*-(2-Phenylethenyl)benzoate (5a). To a 5.0 mM aqueous solution of **5a** (15 mL) was added 20 mg of Kyowaad 2200 clay in a 30-mL Pyrex tube, and the intercalation and irradiation were carried out similar to those for **1a**. The HPLC (detected at 250 nm) analysis of the reaction mixture treated with CH_2N_2 showed four components. Products, retention times (min), and yields (%): methyl ester of *cis*-**5a**, 6.0, and 6; methyl ester of *trans*-**5a**, 6.5, and 2; dimer A, 30, and 65; dimer B, 20, and 27. The dimers A and B were isolated by a SiO_2 column chromatography using CH_2Cl_2 and cyclohexane (25:1). Dimers A and B were characterized to be syn head-to-head (**6a**) and syn head-to-tail dimers (**7a**), respectively, from the following spectral data. Syn head-to-head dimer (**6a**): NMR (δ) carbomethoxy methyl protons (3.8, s, 6 H), cyclobutane methine protons (4.53, oct, 4 H), aromatic protons (7.0–7.2, m, 14 H; 7.8, d, J = 8 Hz, 4 H); MS, *m/e* (relative intensity), 476 (M^+, <1), 445 ($M^+ - OCH_3$, 2), 238 ($M^+/2$, 100), 207 ($M^+/2 - OCH_3$, 7), 179 ($M^+/2 - CO_2CH_3$, 13); λ_{max}(in MeOH, nm) (ϵ), 242 (25 400), 211 (23 700). Syn head-to-tail dimer (**7a**): NMR (δ) carbomethoxy methyl protons (3.8, s, 6 H), cyclobutane methines (4.53, s, 4 H), aromatic protons (7.0–7.2, m, 14 H; 7.8, d, J = 8 Hz, 4 H); MS; *m/e* (relative intensity) 476 (M^+, <1), 445 ($M^+ - OCH_3$, 1), 238 ($M^+/2$, 100), 207 ($M^+/2 - OCH_3$, 1), 179 ($M^+/2 - CO_2CH_3$, 3); λ_{max}(in MeOH, nm) (ϵ), 250 (30 600), 211 (26 800).

Irradiation of Clay-Intercalated 5b. The intercalation and irradiation of sodium *p*-[2-(*p*′-chlorophenyl)ethenyl]benzoate (**5b**) were carried out using methods similar to those observed for the case of **5a**. The HPLC analysis of the reaction mixture treated with CH_2N_2 showed four components. Products, retention times (min), and yield (%): methyl ester of *cis*-**5b**, 5.2, and 1; methyl ester of *trans*-**5b**, 5.5, and 3; dimer C, 21.3, and 87; dimer D, 12.2, and 6. Dimers C and D were isolated by a SiO_2 column chromatography eluting with CH_2Cl_2. Dimers C and D were characterized to be syn head-to-head (**6b**) and syn head-to-tail dimers (**7b**), respectively, from the following spectral data. Syn head-to-head dimer (**6b**): NMR (δ) carbomethoxy methyl protons (3.90, s, 6 H), cyclobutane methine protons (4.45, s, 4 H), aromatic protons (7.01, d, J = 8.7 Hz, 4 H; 7.10, d, J = 8.3 Hz, 4 H; 7.16, d, J = 8.7 Hz, 4 H; 7.79, d, J = 8.3 Hz, 4 H); MS, *m/e* (relative intensity) 544 (M^+, trace), 513 ($M^+ - OCH_3$, 1), 296 ($p\text{-}CH_3O_2CC_6H_4CH{=}CH{-}C_6H_4CO_2CH_3\text{-}p'$, 0.4), 272 ($M^+/2$, 100), 248 ($p\text{-}ClC_6H_4{-}CH{=}CH{-}C_6H_4Cl\text{-}p$, 1), 241 (23), 237 (2), 213 (10), 178 (39). Syn head-to-head dimer (**7b**): NMR (δ) carbomethoxy methyl protons (3.90, s, 6 H), cyclobutane methine protons (4.45, s, 4 H), aromatic protons (7.01, d, J = 8.7 Hz, 4 H; 7.10, d, J = 8.3 Hz, 4 H; 7.16, d, J = 8.7 Hz, 4 H; 7.79, d, J = 8.3 Hz, 4 H); MS, *m/e* (relative intensity) 544 (M^+, trace), 513 ($M^+ - OCH_3$, 2), 272 ($M^+/2$, 100), 241 (23), 237 (2), 213 (7), 178 (40).

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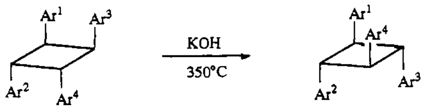
Irradiation of Sodium *p*-(2-Phenylethenyl)benzoate (5a) Cointercalated with Sodium *p*-Phenethylbenzoate (8). To an aqueous clay suspension (5.0 mM) intercalated by a variable amount of sodium *p*-phenethylbenzoate (**8**) (0–5.0 mM) was added an appropriate amount of sodium *p*-(2-phenylethenyl)benzoate (**5a**), keeping the total amount of intercalants at 5.0 mM. The resulting cointercalated samples were irradiated for 4 h. After almost completion of the reaction over 90%, the reaction mixtures were analyzed by HPLC. The results are shown in Figure 3.

Epimerization of Cyclodimers 6a and 7a. The structures of **6a** and **7a** were ascertained by the following epimerization. To a 100-mg quantity of cyclodimer **6a** or **7a** was added 1 g of KOH pellets, and the reaction mixture was heated at around 350 °C for 1 h.[17] After completion of the reaction, the reaction mixture was acidified with concentrated HCl and extracted with ethyl ether. The extract was then treated with CH_2N_2 and purified by passing through a SiO_2 column eluting with CH_2Cl_2. Cyclodimers obtained from epimerization of **6a** and **7a** were identified as the corresponding anti head-to-head (**8a**) and anti head-to-tail dimers (**9a**), respectively, on the basis of the following spectral data. **8a**: NMR (δ) cyclobutane methine protons (3.75, s, 4 H), carbomethoxy methyl protons (3.9, s, 6 H), aromatic protons (7.2–7.4, m, 14 H; 8.0, d, J = 8 Hz, 4 H); MS, *m/e* (relative intensity) 476 (M^+, trace), 445 ($M^+ - OCH_3$, 2), 296 (p-$CH_3O_2CC_6H_4CH{=}CH{-}C_6H_4CO_2CH_3$-$p'$, 7), 265 ($CH_3O_2CC_6H_4CH{=}CH{-}C_6H_4CO$, 2), 238 ($M^+/2$, 75), 207 ($M^+/2 - OCH_3$, 4), 180 ($C_6H_5CH{=}CHC_6H_5$, 100). **9a**: NMR ($\delta$) cyclobutane methine protons (3.75, s, 4 H), carbomethoxy methyl protons (3.9, s, 6 H), aromatic protons (7.2–7.4, m, 14 H; 8.0, d, J = 8 Hz, 4 H); MS, *m/e* (relative intensity) 476 (M^+, trace), 445 ($M^+ - OCH_3$, 1), 238 ($M^+/2$, 100), 207 ($M^+/2 - OCH_3$, 6), 179 ($M^+/2 - CO_2CH_3$, 11). As apparent, the head-to-head-type **6a** could be substantiated by the fragment ions of *m/e* 180 and 296 from **8a** and the head-to-tail-type **7a** by the single major component of $M^+/2$ from **9a**.



(4)

6a, $Ar^1 = Ar^3 = C_6H_5$, $Ar^2 = Ar^4 = C_6H_4CO_2Me$ **8a**, $Ar^1 = Ar^3 = C_6H_5$, $Ar^2 = Ar^4 = C_6H_4CO_2Me$

7a, $Ar^1 = Ar^4 = C_6H_5$. $Ar^2 = Ar^3 = C_6H_4CO_2Me$ **9a**, $Ar^1 = Ar^4 = C_6H_5$, $Ar^2 = Ar^3 = C_6H_4CO_2Me$

HPLC analysis monitored at 250 nm showed the following retention times at a flow rate of 2.5 mL/min: 18.1, 11.8, 12.6, and 11.0 min for **6a**, **7a**, **8a**, and **9a**, respectively.

Determination of Emission Spectra from Intercalated 5a. Clay-intercalated samples were prepared by mixing aqueous solutions of a mixture of **5a** and **8** in a total concentration of 5.0 mM with slight excess amounts of the clay powders and stirring overnight at 60 °C using a Kaijo Denki 200A homogenizer. The suspended solutions were filtered using a membrane filter (Toyo Roshi Co., pore size 0.45 μm), and the filtrated clays were dried in vacuo at room temperature for a few days. The resulting powder samples were filled in a quartz optical cell (10 mm in diameter) and subjected to diffuse reflectance fluorescence spectrophotometry using the Hitachi fluorescence instrument in which optical cell was adjusted 60° against the incident excitation light path.

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