Organized Photocycloaddition of 4-Benzoylbenzoate with Unsaturated Carboxylates in Hydrotalcite Clay Interlayers

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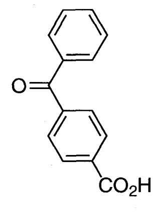
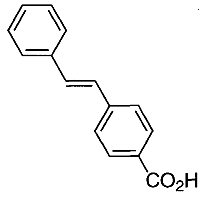
Photoirradiation of a mixture of 4-benzoylbenzoate (**1**) and 4-(2-phenylethenyl)benzoate yielded regioselective oxetanes in the presence of hydrotalcite clay. Similar irradiation of a mixture of **1** and cinnamate gave rise to β-truxinate, but not oxetane. The unexpected formation of oxetanes is understood by the favorable distance between C=O and C=C bonds packed in clay interlayers.

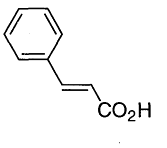
Spatially restricted photochemistry in heterogeneous systems is now one of the most important subjects in relation to various fields such as photocatalytic reactions, photofunctional materials, bio- or environmental photochemistries.[1] In the previous papers, the authors have disclosed photocyclodimerizations of various ionic olefins incorporated in interlayers of clay minerals which possess a layered structure and ion exchange ability.[2-4] The most interesting point in the clay-intercalated photocyclodimerizations is that the stereochemistry of the cyclodimers reflects clearly the orientation of adsorbed ionic olefins. The present article discloses a regioselective photocycloaddition and a sensitized cyclodimerization of unsaturated carboxylates with 4-benzoylbenzoate intercalated in anionic-exchange-clay, hydrotalcite.[5]



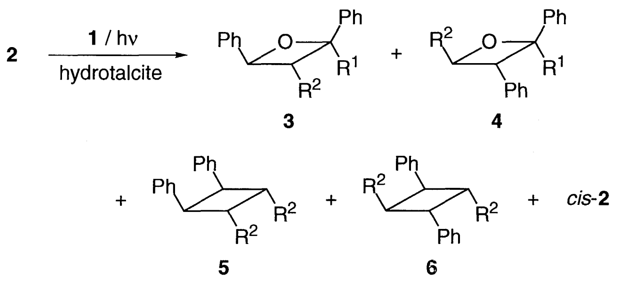
1



2a



2b



$R^1 = C_6H_4CO_2H$ a) $R^2 = C_6H_4CO_2H$
b) $R^2 = CO_2H$

Intercalation of carboxylates, **1** and **2**, was carried out by adding clay powders to aqueous solution of their sodium salts and then stirring at 60 °C for one night. The aqueous suspension was irradiated for 4 hours using a 300 W medium pressure mercury lamp and a Pyrex vessel under Ar atmosphere. The clay suspension was then acidified by conc. HCl, and photoproducts were extracted with ether and methylated with diazomethane. Results of the photoreactions are summarized in Table 1. Products were characterized on the basis of spectroscopic data (^1H, ^{13}C NMR and MS) and analyzed by GLC or HPLC.

Clay-intercalated photoreaction of 4-benzoylbenzoate **1** and 4-(2-phenylethenyl)benzoate **2a** gave rise to unique [2+2]

Table 1. Photoreactions of **1** and unsaturated carboxylates in clay interlayers

run		Concentration (mmol dm^{-3})			Condition	Conv.[b] (%)	Selectivity[c] (%)			
		1	**2**	clay[a]			**3**	**4**	cyclodimer(s)[d] (**5** + **6**)	cis-**2**
1	**2a**	2.5	2.5	5.3	> 280 nm	70	24	2	45[e]	20
2		1.3	3.7	5.3	> 280 nm	50	30	3	45[e]	10
3		2.5	2.5	0	> 280 nm	90	0	0	10[e]	90
4		0	5.0	5.3	> 280 nm	99	0	0	97[e]	3
5	**2b**	2.5	2.5	5.3	> 320 nm	71	0	0	40[f]	60
6		0	5.0	5.3	> 320 nm	0	0	0	0	0
7		2.5	2.5	0	> 320 nm	82	0	0	0	100
8		0	5.0	5.3	> 280 nm	92	0	0	46[f]	54

[a] Concentrations of clay were calculated from anion-exchange capacity of hydrotalcite (AEC; 3.5 meq./g). [b] Conversions of olefins. [c] Selectivities are based on converted olefins. [d] Cyclodimers of olefins. [e] The ratios of syn-HH (**5a**) and syn-HT dimers (**6a**) were varied with conditions, which were roughly estimated to be 4.5 : 1 (runs 1 and 2), 1 : 2 (run 3), and 3 : 1 (run 4) by ^1H-NMR spectra. [f] Syn-HH dimer **5b**.

cycloaddition. Two isomeric oxetanes,[6, 7] cis-head-to-head **3a** and cis-head-to-tail **4a**, were produced in addition to cyclodimers (**5a** and **6a**),[4, 8] cis-olefin, and several minor products (runs 1 and 2). It is known that excited benzophenone produces no cycloadduct with stilbenes which are electrophilic and have low triplet excitation energy.[9] In fact, photoirradiation of a homogeneous solution of **1** and **2a** resulted in no oxetane formation (run 3). Therefore the present formation of oxetanes is a novel photoreaction observable only in clay interlayers. Since the absorption spectrum of **2a** overlaps with that of **1** among most uv region, significant amounts of cyclodimers of olefins (**5a** and **6a**) were also produced directly from excited **2a**. In the case of cinnamate **2b**, such a cycloadduct between **1** and **2b** was not produced. Irradiation of clay-intercalated mixtures of **1** and **2b** resulted in the formation of β-truxinate (**5b**) and the cis-olefin (run 5). Control experiments without **1** or clay (runs 6 and 7) showed that the photoconversion of **2b** is initiated by sensitization with excited **1** and that hydrotalcite interlayers are indispensable for the cyclodimerizations.

One of important factors for the oxetane formation is the spatial alignment of C=O and C=C bonds along *c* axis of hydrotalcite layer, i.e., the coincidence of their heights from the layer surface. In the interlayers, two types of molecular arrangements, HH and HT pairings, are possible (Figure 1). In the case of **1** and **2a** (Figure 1A), their double bonds are located in the approximately same height, so that cycloaddition reaction would facilely take place. On the contrary, distances between C=C bond of **2b** and C=O bond of **1** are more than 4 Å from the in both HH and HT pairing (Figure 1B), and therefore the oxetane formation is less feasible, the sensitized cyclodimerization of **2b** occurring predominantly. The stereoselection of oxetanes (**3a** and **4a**) would be explained by electronic property of **2a** as well as the spatial restriction. On assuming the simplest mechanism via n-π* excited **1**, addition of the carbonyl oxygen occurs at the olefinic carbon possessing high electron density. The electron densities of two olefinic carbons of **2a** were calculated to be -0.093 for the carbon atom of carboxylate side and -0.268 for the other one.[10] The large difference may explain the predominant formation of HH oxetane (**3a**).

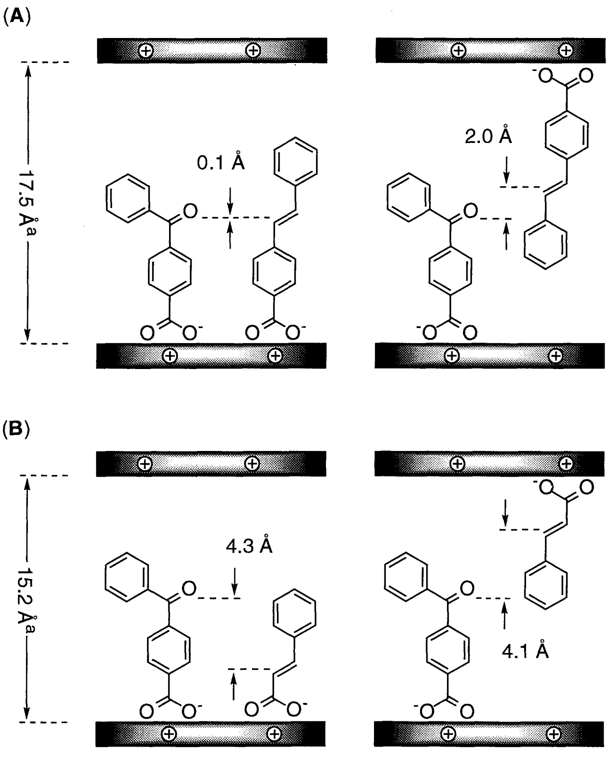


Figure 1. Molecular aggregation models of **1** and **2** in hydrotalcite clay interlayers. HH and HT pairings of (A) **1** and **2a**; (B) **1** and **2b**.

[a] Gallery heights were determined by powder XRD analyses.

In conclusion, we observe a regioselective photocycloaddition of **1** and **2a** giving oxetanes. The efficiency of the cycloaddition is proposed to be controlled by the position of the two double bonds.

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References and Notes

1 J. K. Thomas, *Chem. Rev.,* **80,** 283 (1980); V. Ramamurthy, *Tetrahedron,* **42,** 5753 (1986).

2 R. E. Grim, Clay Mineralogy, McGraw-Hill, New York, (1953).

3 K. Takagi, H. Usami, H. Fukaya, and Y. Sawaki, *J. Chem. Soc., Chem. Commun.,* **1989,** 1174; H. Usami, K. Takagi, and Y. Sawaki, *J. Chem. Soc., Perkin Trans. 2,* **1990,** 1723.

4 K. Takagi, T. Shichi, H. Usami, and Y. Sawaki, *J. Am. Chem. Soc.,* **116,** 4339 (1993).

5 S. Miyata, *Gypsum & Lime,* **187,** 47 (1983).

6 Structural assignment of **3a** was confirmed by mass spectra. Characteristic fragment ions, m/z 372 of 1,2-di(*p*-methoxycarbonylphenyl)-1-phenylethene and m/z 106 of benzaldehyde, indicate HH structure. Stereochemical structure was deduced by NOE experiments which showed that two protons attached on the 4-membered ring and two methoxycarbonylphenyl groups have trans and cis configurations, respectively. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.85 (4H, d, J=8.4 Hz), 7.52 (2H, d, J=8.2 Hz), 7.41 (2H, t, J=8.2 Hz), 7.35-7.25 (8H, m), 7.14 (2H, d, J=8.4 Hz), 6.00 (1H, d, J=8.2 Hz), 4.88 (1H, d, J=8.2 Hz), 3.89 (3H, s), 3.88 (3H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 167.1, 166.9, 147.0, 146.9, 141.4, 140.9, 129.7, 129.4, 129.2, 128.8, 128.7, 128.5, 127.6, 126.4, 125.8, 124.9, 88.8, 82.2, 60.7, 52.1, 52.0; MS (EI, 70 eV) m/z (relative intensity) 372 (36), 254 (22), 253 (21), 252 (18), 239 (21), 238 (100), 207 (18), 179 (40), 178 (30), 155 (14), 126 (23), 113 (13), 106 (30), 105 (42).

7 HT structure of **4a** was determined by detecting fragment ions, m/z 314 of 1-*p*-methoxycarbonylphenyl-1,2-diphenylethene and m/z 164 of *p*-methoxycarbonyl-benzaldehyde. Configurations were tentatively assigned as shown in scheme because of the fact that a shielding effect by adjacent aromatic ring was observed only for one methoxycarbonylphenyl group. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.97 (2H, d, J=8.4 Hz), 7.39 (2H, d, J=8.4 Hz), 6.01 (1H, d, J= 8.2 Hz), 4.71 (1H, d, J=8.2 Hz), 3.89 (3H, s), 3.87 (3H, s); MS (EI, 70 eV) m/z (relative intensity) 314 (43), 313 (11), 255 (22), 254 (12), 253 (16), 252 (14), 240 (13), 239 (30), 238 (100), 225 (13), 207 (14), 179 (46), 178 (40), 165 (12), 164 (26), 163 (22), 133 (48), 126 (15), 105 (37).

8 A mixture of syn-HH (**5a**) and syn-HT (**6a**) in a ratio of ca. 4.5 : 1.

9 D. R. Arnold, *Advan. Photochem.,* **6,** 301 (1968).

10 Gaussian 94 RHF/PM3.