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Intercalation and control of the Norrish type II reactions of aromatic ketocarboxylates in hydrotalcite clay interlayers

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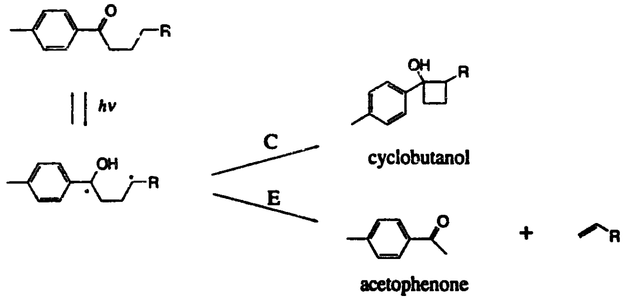
Abstract

The Norrish type II reactions of a number of aromatic ketocarboxylate ions, p-$CH_3C_6H_4CO(CH_2)_nCO^{2-}$ (**1**, $n=4$–10), were studied under the conditions of intercalation in the anion-exchange clay, hydrotalcite. Photolysis of **1** adsorbed in aqueous hydrotalcite suspension yielded the type II products p-methylacetophenone and alkenecarboxylates (E), and/or cyclobutanols (C) in variable yields depending on the length of the alkyl chains (n). The ratios C/E decreased with increasing n and hence became negligibly small when $n \geq 6$, in contrast with the photolysis of **1** in homogeneous aqueous solutions. The effect of coadsorbates was significant in the acceleration of the type II reaction, but the product distributions remained unchanged. These results will be discussed in terms of the conformational flexibility of the aromatic ketocarboxylate ions imposed by the interlayer space of hydrotalcite clays. © 1997 Elsevier Science S.A. All rights reserved.

Keywords: Hydrotalcite; Intercalation; Norrish type II reactions

1. Introduction

In recent decades, increasing effort and interest have been focussed on photochemistry in organized environments [1,2]. This is largely because organized photochemistry is intimately related to wide fields of investigations, e.g. photocatalytic reactions [3], photofunctional materials [4], and solar energy storage [5], concerning various photonic devices. The Norrish type II reaction of aromatic ketones has been extensively studied and is often applied as a probe reaction for studying various kinds of organized anisotropic systems, such as micelles [6], vesicles or LB membranes [7], liquid crystals [8], and zeolites [9]. In type II reactions, the intermediary 1,4-biradicals from the excited triplet state formed via intramolecular γ-hydrogen abstraction lead to cyclization to cyclobutanol (C) or elimination to olefin and ketone (E), competing with reverse hydrogen transfer in the biradical, as depicted in Scheme 1. Hence, the efficiency of product formation and the ratios of cyclization (C) to elimination products (E) are well known to be significantly sensitive to the environment in which the ketone molecules are accommodated. Indeed, the type II photoreactions of ketones are known to be influenced by their conformational flexibilities [10], as well as solvent polarity [11], temperature [12], and substituents [13].



Scheme 1. The Norrish type II reacion of aromatic ketones with γ-hydrogen.

In the case of the solution photolysis of valerophenone, a typical aromatic ketone, the quantum efficiency of the type II reaction is about half as much in non-polar solvents (e.g. hexene) as it is in polar ones (e.g. acetonitrile), but the cyclobutanol (C) is formed in about 15% of the ketone reactions irrespective of the kind of solvent [11]b. This implies that polar solvents accelerate the decomposition of ketone owing to the stabilization of the intermediary 1,4-biradicals by solvation effects, but have little influence on the ratio C/E. In addition, the reactivity is also influenced strongly by conformational flexibility in the molecules [10]. Conformational changes of the 1,4-biradicals evidently control the ratio of elimination (E) or cyclization products (C) when the type II reaction is carried out in some anisotropic media, such as liquid crystalline solvents [14,15]. Whitten and co-

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workers [16] have reported that surfactant ketocarboxylates, ω-(*p*-toluoyl)alkanoates (**1**), are subject to the type II reaction with changeable reactivities depending on micelles and vesicles as reaction media. However, a multilayer of assemblies of **1** exhibits very little type II reactivity with $\Phi < 0.01$, although the usual reactivity was observed in the cases of micelles similar to homogeneous solutions.

We have undertaken a study on the Norrish type II reaction of aromatic ketocarboxylates intercalated in hydrotalcite clay in order to examine whether the layer space controls the reaction course by restriction of the conformational mobility of 1,4-biradicals. Clays can accommodate various molecular species, charged or neutral, in the interlayers [17–19], and intercalations of guest molecules in clays are mostly based on electrostatic interactions between ionic guest molecules and the ionic sites of interlayer surfaces. Sometimes, steric restrictions are found to be imposed on the intercalated guest ions. Herein, we report interesting features of the type II photoprocess of aromatic ketocarboxylates (**1**) in the interlayers.

2. Materials and methods

UV and visible spectra were recorded on a Shimadzu UV-265 spectrophotometer. GLC analyses were done with a Yanagimoto G180 gas chromatograph using a 1 or 2 m column of carbowax 300 M at 50–250 °C. NMR spectra were taken with a Varian Jemini-200 NMR instrument. Mass spectra were measured with a JOEL high resolution mass spectrometer (Model D-300) employing a direct inlet system; 20 eV ionization potential. X-ray powder diffraction analysis was carried out using an X-ray diffractometer (Rigaku Denki) with Ni-filtered Cu–Kα radiation. The 003 basal spacings of the layers were measured by the Debye–Scherrer method. The melting points are corrected.

2.1. Materials

ω-(*p*-Toluoyl)butanoic acid ($n = 3$) was synthesized by treating *p*-tolylmagnesium bromide with glutaric anhydride according to the procedure reported by Weizmann et al. [22]: colorless crystal (after recrystallization from hexane–ethanol) mp 155–156 °C; m/z 220 (M^+, 6), 207 (3), 189 (9), 161 (6), 134 (12), 119 (100), 91 (30); NMR ($CDCl_3$) δ 2.0 (m, 2H), 2.4 (s, 3H), 2.5 (t, 2H), and 7.2–7.8 (m, 4H). ω-(*p*-Toluoyl)pentanoic (**1a**, $n = 4$), -hexanoic (**1b**, $n = 5$), -heptanoic (**1c**, $n = 6$), and -nonanoic acid (**1d**, $n = 8$) were synthesized by the Friedel–Crafts reaction of the corresponding 1,ω-alkanedicarboxylic acid dichlorides with toluene in the presence of anhydrous aluminum chloride, followed by hydrolysis by sulfuric acid according to the known procedures [22]. ω-(*p*-Toluoyl)pentanoic acid (**1a**, $n = 4$): mp 153.0–155.4 °C; m/z 220 (M^+, 1), 202 (4), 187 (1), 174 (2), 134 (62), 119 (100), 91 (7); NMR ($CDCl_3$) δ 1.7 (m, 4H), 2.3 (s+m, 7H), 2.9 (t, 2H), and 7.0–7.8 (m, 4H). Anal. calc. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.79; H, 7.4. ω-(*p*-Toluoyl)hexanoic acid (**1b**, $n = 5$): mp 137–139.5 °C; its methyl ester, m/z 248 (M^+, < 1), 230 (5), 171 (4), 134 (58), 119 (100), 91 (30); NMR ($CDCl_3$) δ 2.0 (m, 2H), 2.4 (s, 3H), 2.5 (t, 2H), and 7.2–7.8 (m, 4H). Anal. calc. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.66; H, 8.37. ω-(*p*-Toluoyl)heptanoic acid (**1c**, $n = 6$): mp 106.4–107.3 °C; its methyl ester, m/z 262 (M^+, < 1), 244 (3), 213 (1), 147 (17), 134 (100), 119 (69), 91 (33); NMR ($CDCl_3$) δ 1.4 (m, 4H), 1.7 (m, 4H), 2.3 (t, 2H), 2.4 (s, 3H), 2.9 (t, 2H), and 7.2–7.9 (m, 4H). ω-(*p*-Toluoyl)nonanoic acid (**1d**, $n = 8$): mp 95.0–96.5 °C; m/z 276 (1), 258 (1), 243 (< 1), 147 (8), 134 (100), 119 (61), 91 (3); NMR ($CDCl_3$) δ 1.3 (m, 8H), 1.6 (m, 4H), 2.3 (t, 2H), 2.4 (s, 3H), 2.9 (t, 2H), and 7.2–7.9 (m, 4H). Anal. calc. for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.23; H, 8.71. ω-(*p*-Toluoyl)undecanoic acid (**1e**, $n = 10$) was prepared by ozonolysis of 1-(*p*-toluoyl)cyclododecene in methanol, followed by hydrolysis to the free acid by KOH [20]: mp 87.3–88.7 °C; m/z 304 (M^+, 1), 286 (1), 271 (1), 147 (5), 134 (100), 119 (19); NMR ($CDCl_3$) δ 1.3 (m, 12H), 1.4–1.8 (m, 12H), 2.3 (t, 2H), 2.4 (s, 3H), 2.9 (t, 2H), and 7.2–7.9 (m, 4H). ω-(*p*-Tolyl)hexanoic and -decanoic acid were synthesized by the reduction of **1a** and **1c** with hydrazine according to the known procedure [23]. Other carboxylic acids were commercially available and used without further purification.

The hydrotalcite clays Kyowaad 2200 and Alcamac were gifted by Kyowa Chemicals Ltd. The former is an anhydrous metal oxide, $(Al_2O_3)(MgO)_{4.5}$, and the latter is the hydrated form containing chloride ions in the interlayers, i.e. $[Al_2Mg_{4.5}(OH)_{13}]Cl_2 \cdot 4H_2O$. The AECs (anion-exchange capacity) of Kyowaad 2200 and Alcamac are 705 and 350 meq/100 g, respectively.

2.2. Intercalation on clay

Clay-intercalated samples were prepared by mixing 1.0–10 mM aqueous solutions of unsaturated carboxylates with slightly excess amounts of the clay powder and stirring overnight at 50 °C using a Kaijo Denki 200A homogenizer. After cooling 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.

2.3. Equilibrium constants, K_{ad}, for intercalation

After stirring overnight at 50 °C in order to attain equilibrium, the 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 filterate. The equilibrium constants for the

Table 1
Adsorption behavior of aromatic ketocarboxylates (**1**) in the treatment with Alcamac, $[Al_2Mg_{4.5}(OH)_{13}]Cl_2 \cdot 4H_2O$, with an AEC of 350 mequiv/100 g

Ketocarboxylate	Degree of adsorption (%) [a]	Equilibrium constant (K_{ad}) [b]	Gallery height (Å) [c]	Molecular length of **1** (Å)
None	–	–	2.9	–
1a ($n = 4$)	68	4.52	22 ± 2	13.6
1b ($n = 5$)	71	5.99	23 ± 3	14.8
1c ($n = 6$)	77	11.2	26 ± 2	16.1
1d ($n = 8$)	88	53.8	25 ± 3	18.1
1e ($n = 10$)	92	132	25 ± 2	21.2

[a] Intercalation of ketocarbocylates was performed by stirring an aqueous suspension of a mixture of **1** and Alcamac each at a concentration of 7.0 mM for 12 h at 50 °C. The % adsorptions are based on the AEC.

[b] According to Eq. (1).

[c] The 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.

intercalation on hydrotalcite interlayers were calculated according to Eq. (1) and are listed in Table 1.

2.4. Irradiation of sodium ω-(p-toluoyl)alkanoates (1a–1e) with hydrotalcite clay

To a 15 ml aqueous solution of 7 mM sodium ω-(*p*-toluoyl)alkanoates (**1**) was added 20 mg of hydrotalcite clay powder, Kyowaad 2200, in a 30 ml quartz tube with a septum cap, and the mixture was stirred overnight at 50 °C. The reaction suspension was cooled to room temperature, filtered by a membrane filter with a pore size of 0.45 μm (Advantec, Toyo Roshi Ltd.), and dried under vacuo overnight to give a colorless powder. An aqueous suspension of the resulting powder was irradiated by a Hg arc lamp (300 W) through a pyrex filter under magnetic stirring. Argon gas was bubbled through before irradiation. After the reaction, the suspension was acidified with concentrated HCl (15 ml) 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, dried over anhydrous Na_2SO_4, and was then condensed in vacuo to give a pale yellow oil. The products were analyzed by GLC and compared with authentic samples prepared independently. *p*-Methylacetophenone and a series of methyl ω-alkenoates ($n = 4$, 5, 6, 8, and 10) were commercially available and used as the authentic samples. A mixture of approximately equal amounts of *cis*- and *trans*-cylobutanols (**3**) was obtained by photolysis of the methyl esters of a series of ketocarboxylates (**1**) in acetonitrile. *cis*-**3a** was isolated as the corresponding lactone by intramolecular esterification during the work-up procedure after UV irradiation; NMR (δ) 1.88, m, 1H; 2.33, s, 3H; 2.34, m, 1H; 2.48–2.88, m, 4H; 3.23, q, 1H; 7.1–7.3, m, 4H; IR (cm^{-1}) 1771; mass (*m*/*z*), 202 (M^+, 3), 187 (23), 174 (38), 134 (9), 119 (100), 91 (3). *trans*-**3a**, mass (*m*/*z*), 216 (M^+-18, 20), 187 (6), 185 (3), 174 (8), 158 (17), 157 (80), 156 (23), 142 (100), 141 (41), 134 (34), 129 (25), 128 (28), 119 (42), 115 (36). **3b**, 230 (M^+-18, 31), 199 (7), 198 (5), 171 (13), 170 (23), 159 (7), 158 (14), 157 (100), 156 (91), 155 (43), 143 (41), 142 (51), 141 (56), 134 (39), 129 (31), 128 (48), 119 (30). **3c**, 244 (M^+-18, 28), 213 (10), 212 (5), 197 (5), 188 (3), 185 (4), 184 (10), 171 (20), 170 (83), 169 (31), 158 (16), 157 (100), 155 (75), 154 (11), 143 (52), 142 (63), 141 (46), 134 (57), 129 (43), 128 (45). Authentic samples of methyl ω-[2-hydroxy-2-(*p*-tolyl)cyclobutyl]octanoate (**3**, $n = 12$): *cis*-**3d**; NMR (δ) 1.1–1.7, 12H, methylene; 1.8, m, 1H; 1.95, m, 1H, methine of cyclobutane; 2.15, m, 1H, methine of cyclobutane; 2.28, t, 2H, CH_2CO_2; 2.32, s, 3H, aromatic methyl; 2.38, m, 1H, methine of cyclobutane; 2.59, m, 1H, methine of cyclobutane; 3.6, s, 3H, ester methyl; 7.1–7.4, m, 4H, aromatic protons; mass (*m*/*z*), 318 (M^+, 8), 275 (21), 244 (20), 216 (23), 161 (45), 134 (39), 119 (100), 105 (54), 89 (49). *trans*-**3d**; NMR (δ) 0.8–1.7, 12H, methylene; 1.9–2.7, m, 5H; 2.24, t, 2H, CH_2CO_2; 2.33, s, 3H, aromatic methyl; 3.64, s, 3H, ester methyl; 7.1–7.4, m, 4H, aromatic protons; mass (*m*/*z*), 318 (M^+, trace), 300 (11), 171 (22), 157 (100), 143 (23), 119 (9), 83 (8). Authentic samples of methyl ω-[2-hydroxy-2-(*p*-tolyl)cyclobutyl]pentanoate: trans isomer as a lactone; NMR (δ) 1.88, m, 1H; 2.33, s, 3H, aromatic methyl; 2.34, m, 1H, methine of cyclobutane; 2.48–2.88, m, 4H; 3.23, q, 1H; 7.1–7.3, m, 4H, aromatic protons; mass (*m*/*z*), 202 (M^+, 3), 187 (23), 174 (38), 134 (9), 119 (100), 91 (3); IR (liquid film), 1771 cm^{-1}.

3. Results

3.1. Intercalation of aromatic ketocarboxylates (1) in hydrotalcite clay

Aromatic ketocarboxylates (**1**) were intercalated by ion exchange with anions incorporated in clay interlayers. The hydrotalcites employed as anion-exchange clays in the present work were Kyowaad 2200 and Alcamac, manufactured by Kyowa Chemicals Ltd., which are layered minerals composed of an octahedral $Mg(OH)_2$ and exchangeable anion as shown in Fig. 1. Kyowaad 2200 is an anhydrous metal oxide, $(Al_2O_3)(MgO)_{4.5}$, and is converted on hydration to a hydrotalcite-like intercalate containing interlayer OH^- ions; its anion-exchange capacity (AEC) is 705 mequiv/100 g.

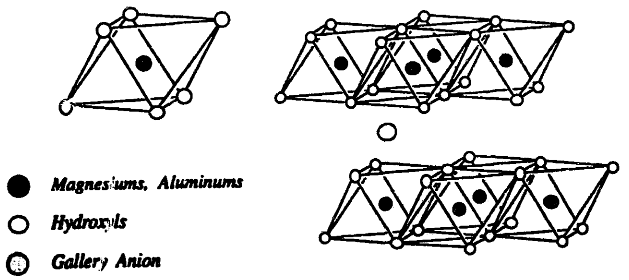
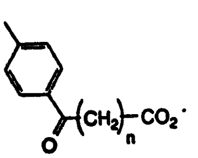


Fig. 1. A structure of hydrotalcite clay: an octahedral of $Mg(OH)_2$ (left) and a layered structure composed of octahedral $Mg(OH)_2$ (right) including gallery ion such as Cl^- or OH^-.

Alcamac is a hydrated hydrotalcite containing chloride anions 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.



a (n=4)
b (n=5)
c (n=6)
d (n=8)
e (n=10)

1

The degree of intercalation of 1 may be expressed by the following equilibrium equation (Eq. (1)), where $RCO^{2-}clay^+$ denotes the intercalated carboxylate. The degree of intercalation was determined by measuring the carboxylates filtrated through a membrane filter from aqueous solutions of a 1:1 mixture of carboxylate and clay, and the equilibrium constants were calculated according to Eq. (2) and are listed in Table 1.

$$\mathrm{RCO_2^-Na^+ + clay^+Cl^- \overset{K_{ad}}{\rightleftarrows} RCO_2^-clay^+ + Na^+Cl^-} \quad (1)$$

$$K_{ad} = \frac{[\mathrm{RCO_2^-clay^+}][\mathrm{Na^+Cl^-}]}{[\mathrm{RCO_2^-Na^+}][\mathrm{clay^+Cl^-}]} \quad (2)$$

3.2. Sample preparation and photolysis

An aqueous suspension of hydrotalcite clay, Kyowaad 2200 (7.0 mM on the basis of anion-exchange capacity) was mixed with 7.0 mM sodium ω-(p-toluoyl)alkanoates, p-$CH_3C_6H_4CO(CH_2)_nCO^{2-}$ (1), and the suspension was kept stirring overnight at around 50 °C. Ketocarboxylates (1) in the aqueous hydrotalcite suspensions were irradiated with Pyrex-filtered UV light (> 280 nm) under argon. After irradiation, the reaction mixtures were treated by concentrated HCl to decompose the layered structure of the clays, extracted with methylene chloride, and analyzed by GLC after methylation with CH_2N_2 (see Section 2 for details). The observed products were the elimination products (E), p-methylacetophenone (2) and alkenecarboxylates (4), and/or the cyclization product (3), accompanied by a small amount of type I products, p-tolualdehyde (5). As listed in Table 2, the product yields were dependent on the lengths of the alkyl chains.

Cyclobutanols (3) were not obtained for the case of **1c**, **1d**, and **1e** of longer-chain ketocarboxylates intercalated in clay interlayers. This is quite a contrast to the corresponding photoreaction in homogeneous aqueous solutions. Details of these points are noted in Section 4.

Cis- and *trans*-cyclobutanols (3) could not be estimated separately by means of GLC analysis, this being especially

Table 2
The Norrish type II reaction of sodium ω-(p-toluoyl)alkanoates (1) in hydrotalcite clay suspension and in homogeneous water [a]

Ketocarboxylate	Reaction medium	Quantum yield (Φ_{rel})	Selectivity (%)				C/E
			2	3	4	5	
(A) in hydrotalcite interlayer							
1a (n=4)	Aq. clay	(1)	77	20	[b]	[b]	0.26
1b (n=5)	Aq. clay	0.78	84	12	[b]	Trace	0.14
1c (n=6)	Aq. clay	0.70	77	Trace	29	2	0
1d (n=8)	Aq. clay	0.62	78	[b]	55	1	0
1e (n=10)	Aq. clay	0.38	83	[b]	78	Trace	0
(B) in homogenous H_2O							
1a (n=4)	H_2O	(1)	69	25	[b]	[b]	0.36
	t-BuOH	1.01	82	12	[b]	[b]	0.15
1b (n=5)	H_2O	0.89	78	17	[b]	[b]	0.22
1c (n=6)	H_2O	0.74	75	17	30	2	0.23
	t-BuOH	0.86	87	10	44	1	0.11
1d (n=8)	H_2O	1.16	58	33	45	[b]	0.57
	t-BuOH	1.01	80	20	55	[b]	0.25
1e (n=10)	H_2O	1.08	59	33	55	[b]	0.56
	t-BuOH	0.94	80	20	70	[b]	0.25

[a] A 0.25 mM solution of 1 was irradiated with a 300 W Hg lamp through a pyrex filter for 30 min either in the presence or the absence of 0.25 mM clay. Products were determined by GLC analyses.

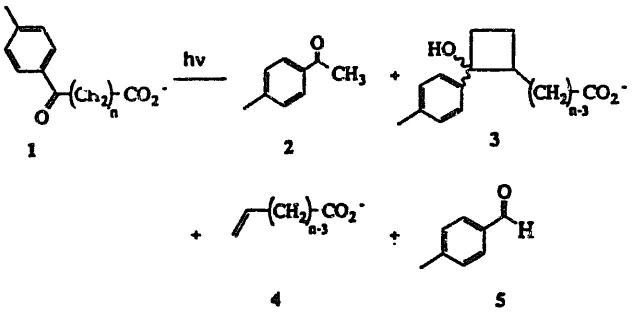
[b] A series of fragment products, ω-alkenic carboxylates (4), were detected using GLC after methylation by CH_2N_2. The yields of some low boiling carboxylates 4 were not estimated owing to overlap of the peak with that of the solvent.

Table 3
Effect of the degree of adsorption onto typical ketocarboxylates (**1a** and **1d**) on the disappearance and product selectivity in their photolysis [a]

Adsorption amounts (%)				Conv. (%)	Selectivity (%)		
Ketocarboxylate [b]		Aliphatic carboxylate [b]			2	3	
1a	(14)	None		26	80	19	
	(28)			29	78	21	
	(53)			33	80	20	
	(64)			29	68	31	
	(8)	Caprate	(79)	79	83	17	
	(14)		(64)	69	81	19	
	(35)		(38)	59	80	19	
	(48)		(19)	54	77	21	
1d	(3)	None		8	87	[c]	
	(7)			7	82	[c]	
	(30)			10	86	[c]	
	(30)			17	73	[c]	
	(64)			25	74	[c]	
	(79)			32	75	[c]	
	(13)	Myristate		(85)	52	81	[c]
	(24)			(70)	51	74	[c]
	(48)			(40)	45	70	[c]
	(63)			(20)	30	71	[c]

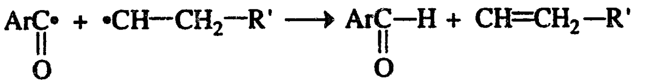
[a] Irradiation for 30 min with a 300 W Hg lamp through a pyrex filter. Concentration of ketocarboxylates: 2.5 mM in 10 ml H_2O.
[b] In parentheses, adsorption amounts of guest molecules (%) based on the cationic sites available on the clay surface are noted.
[c] Several unidentified aromatic compounds except for the cyclobutanols were detected by GLC.

difficult for the case of higher alkyl chain sustituted homologs. Instead, NMR analyses showed the formation of approximately eqaul amounts of cis and trans isomers, and the cis/trans ratios were little affected by the change in chain length. The yields of **3** in Table 2 refer to the total yields of the two isomers.



a, n = 4; b, n = 5; c, n = 6; d, n = 8; e, n = 10

The formation of a small amount of tolualdehyde **5** in the case of **1c** and **1d** implies a competitive type I reaction to yield benzoyl radicals; tolualdehyde is probably produced by hydrogen abstraction from alkyl radicals.



$$\underset{\underset{O}{\|}}{ArC}\bullet + \bullet CH{-}CH_2{-}R' \longrightarrow \underset{\underset{O}{\|}}{ArC}{-}H + CH{=}CH_2{-}R'$$

3.3. *Effect of degree of intercalation*

The effect of the degree of intercalation of the guest **1** on the type II reaction was studied. The layer surface coverage by the guest carboxylates was varied in the range 3–79% by addition of appropriate amounts of clay to a constant amount of **1**. The photochemical conversions were determined under normalized conditions of 2.5 mM of **1** by irradiating for 30 min, suggesting that the figures roughly correspond to apparent quantum efficiencies. Table 3 shows that the conversion of the Type II reaction gradually increased with increasing intercalation percentage of **1d** ($n = 8$), while the reaction of **1a** ($n = 4$) showed little dependence on the degree of intercalation. The product distributions, however, remained unchanged with the wide variation in degree of adsorption in the cases of **1a** and **1d**.

3.4. *Effect of coadsorbate*

Clay interlayers are sometimes modified by the intercalation of ionic surfactant molecules. The resulting modified clays are more dispersed in hydrophobic than in hydrophilic solvents, and may provide a more hydrophobic interlayer space. In order to obtain information on the effect of hydrophobicity on the type II reaction, the present hydrotalcite clay was modified by the intercalation of various sorts of photoinactive carboxylates as coadsorbate (Table 3). The type II reaction was accelerated when aliphatic carboxylates were coadsorbed, and the acceleration was more effective in the case of a higher ratio of **1a** and coadsorbate.

4. Discussion

4.1. *Intercalation of ketocarboxylates*

Most of the ketocarboxylates were adsorbed onto the interlayer surfaces of clay minerals and X-ray diffraction analysis

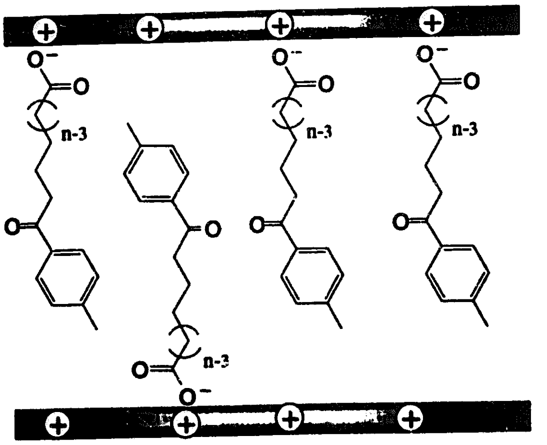


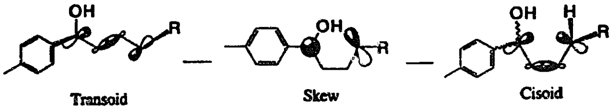
Fig. 2. Intercalation of ketocarboxylate (**1**) in the interlayers of hydrotalcite.

showed that the intercalation broadened the layer space from 3 to 22–26 Å, as shown in Table 1. The external surface area of the clay mineral is less than one-thousandth of the internal one on the basis of average-sized clay particles (around 10 μm) consisting of thousands of stacked layers of thickness 20–30 Å. Judging from the fact that the layer distances of clays containing guest molecules **1** were slightly less than their molecular lengths, it may be reasonable to assume that the guest molecules are packed top to bottom perpendicularly to the layer surfaces to form loose monolayers in the interlayers, as shown in Fig. 2. An analogous alignment was previously proposed on the basis of the stereochemical behavior of the [2+2] photocycloaddition of unsaturated carboxylates [20].

The hydrotalcites employed here consist of stacked sheets of MgO octahedral lattices with central Mg atoms, one-third of which are substituted by Al atoms with a formal positive charge. The cationic Al sites are statistically scattered in every ≈ 30 Å^2 cross-sectional area on the basis of an average distance of 5.4 Å between two adjacent Al atoms. The ketocarboxylate molecules should then be loosely packed in the interlayers since they occupy about 20 Å^2 in their linear structure. These considerations suggest that the molecular packing is not as tight as in the cases of LB membranes or vesicles. The looseness of the packing of the intercalant is supported by the fact that DTA analysis of the guest intercalated clay powder showed water elimination at around 100°C for 6 h, resulting in the compression of layer spaces with the disappearance of X-ray diffraction at an angle of 2.5–3°, as first noticed by Borja and Dutta [21].

4.2. Control of type II photoreaction

Ketocarboxylates intercalated in clay, on UV irradiation, mainly gave the Norrish type II elimination products, *p*-methylacetophenone, alkenecarboxylates (E), and/or the cyclization products, cyclobutanols (C). The formation of cyclized products (C) was substantial for **1a** and **1b** with shorter chain lengths ($n=4$ and 5, respectively), and negligibly small for **1d** and **1e** with longer chain lengths ($n=8$ and 10, respectively), through the intermediate case of **1c** ($n=6$). Type II elimination products (E) are constantly formed as major products throughout $n=4$–10. The results were in contrast with those for the photolysis of **1** in aqueous solutions, which are also included in Table 2. In aqueous solution, the ratios of C to E were almost constant, irrespective of the chain length of **1**. Extremely different results in the cases of clay and homogeneous systems imply that the stereochemistry of 1,4-biradicals is significantly governed by spatial restrictions imposed by the media accommodating **1**. The triplet diradical, the primary product of γ-hydrogen abstraction, is generated in the skew form, and transforms to the transoid and cisoid conformers via rotation of the central σ-bond, as shown in Scheme 2. It is well known that the cyclization products (**3**) (C) may generally be derived from collapse of the cisoid biradical, while the elimination products arise from the transoid biradical [14,15]. Although the cisoid biradical may yield elimination (E) as well as cyclization products (C), depending on the steric constraints imposed and on the presence or absence of alkyl substituents at the γ-carbon in the case without intramolecular constraints, several studies indicate that the vast majority of elimination products arise from the transoid biradical [9]d. This led to the conclusion in the present study that the shorter alkyl chain ketocarboxylates should form cisoid conformers to give cyclobutanols in the interlayers, while the longer ones may be suppressed to cyclize through cisoid owing to the steric hindrance of the bulkier long alkyl chain in the restricted interlayer spaces.



Scheme 2. Plausible conformational change of 1,4-biradicals resulting from the skew conformer formed via intramolecular γ-hydrogen abstraction of an aromatic ketone.

It is proposed that the shorter chain-length ketocarboxylates tend to be rather loosely packed, permitting a more freely mobile cisoid conformation to be taken. However, complete suppression of cyclobutanol formation in the case of the longer chain-length compounds **1d**–**1f** implys that compact packing would be attained in the interlayers, thereby forcing molecular conformations unfavorable either for intramolecular γ-hydrogen abstraction or for transformation of the skew form to a sterically bulkier cisoid diradical. The present results indicate that conformational change may be a key step in the product distribution between cyclobutanols and alkene + aromatic ketone. In fact, the former possibility would be less feasible, because type II fragment products were still formed with rather high quantum efficiency, even in the cases of **1d**–**1f** with higher alkyl chains. Molecular alignment in the restricted layer space resulted in compact aggregate of the guest molecules, which prevents the skew conformer from isomerization to the cisoid form. Nonetheless, the molecular packing would not be so close as to inhibit conformations favorable for γ-hydrogen abstraction.

Additionally, in the case of ω-(p-toluoyl)butanoic acid (**1**, $n=3$) with a γ-hydrogen attached to the carbon atom substituted by the carboxyl group, the type I fragmentation to p-tolualdehyde (**2**) predominated over the type II processes in clay interlayers or in aqueous solution. It is reasonably assumed that cleavage of the carbon–hydrogen bond substituted by the carboxyl group is hard on account of the instability of a 1,4-diradical with an odd electron at the carbon next to the carboxylate group.

Table 2 contains the relative quantum yields (Φ_{rel}) of consumption of the starting ketones. On increasing the chain length of the carboxylates, the quantum yields became lower. It is implied that the aromatic ketocarboxylates (**1**) are packed as anti-parallel monolayers in the interlayers of clay as well as conditions in the interlayers becoming less polar. The extent of alignment of the carboxylates should critically affect the efficiency of type II eliminations. Indeed, tightly packed ketocarboxylate molecules in dioctadecylmethylammonium (DODAC) chloride vesicles exhibit very little type II reactivity ($\phi < 0.01$) [16], and no reaction occurred at all with aromatic ketones more rigidly incorporated into LB membranes [7]. This is because such conditions make it difficult for the ketocarboxylate molecules to abstract intramolecular γ-hydrogen atoms by interacting with the six-membered cyclic transition state. As shown in Fig. 2, ketocarboxylates in the present clay interlayers are proposed to be aligned regularly, but not as compactly as the DODAC membrane. We assume that the longer-chain ketocarboxylates (**1c**–**1e**) would orient themselves more regularly than the shorter chain-length **1a** and **1b**.

4.3. *Effect of degree of adsorption of ketocarboxylates*

As stated above, short alkyl-chain **1a** or **1b** afford cyclobutanols, whereas long alkyl-chain **1c** or **1e** fail to cyclize. This effect was proposed to be due to restricted clay interlayer spaces. In order to get further information on the adsorption behavior of these substrates, we studied the effect of the degree of adsorption of **1** on the efficiency and product distribution. As a typical example, **1a** ($n=4$) and **1d** ($n=8$) were examined in the range 3–79% based on the AEC of clay. Table 3 shows no dependence of product selectivity with respect to the change in the degree of adsorption in both ketocarboxyaltes, i.e. cyclobutanols were formed with **1a** ($n=4$) but not **1d** ($n=8$). It appears incorrect to assume that adsorbed molecules would move further apart from each other with decreasing degrees of adsorption and, therefore, they should be isolated from other guests in order to experience sterically less restricted conditions. The results suggest that organic guest molecules aggregate by themselves at an even lower adsorption percentage, and therefore no cyclization occurred at all. Similar phenomena were found in the photochemical cyclodimerization and excimer/monomer emissions of saponite-supported stilbazolium ions (stz$^+$). Only 1% coverage based on the ionic sites of the interlayer surface with stz$^+$ resulted in efficient photodimerization and excimer emissions, which implies heterogeneous adsorption to form stz$^+$ clusters. In conclusion, the extent of molecular packing is believed not to be affected by changes in the intercalation percentage in the range of 3–79%.

4.4. *Effect of coadsorption of external carboxylates*

Similar to the effect of the degree of adsorption of the guest ketocarboxylates, the type II reactivity was affected by the addition of external coadsorbates for **1a** and **1c**, respectively. Table 3 also indicates an effect of coadsorption on the quantum efficiency of the fragmentation reactions. When clay samples containing variable ratios of ketocarboxylates to external carboxylates were subjected to type II reactions, keeping the total coverage constant (80–90% based on the AEC), the quantum yields were substantially improved (Table 3). This may be explained by the assumption that the regularity of orientation becomes worse with increasing ratio which should lead to higher reactivities.

It is important to differentiate between the mechanistic steps that determine the product ratios and Φ_{rel}. Whereas the C/E ratios depend solely upon the fraction of triplet 1,4-diradicals that eventually give products, Φ_{rel} is a function of all the steps subsequent to ketone excitation. The magnitude of Φ_{rel} is given by the product of the fraction of ketone triplets undergoing hydrogen abstraction and the fraction of those biradicals not participating in back hydrogen transfer. Assuming equal formation of 1,4-diradicals irrespective of the change in chain length, the latter factor is crucial in the determination of the total quantum efficiency of the photoreactivity under rigid conditions such as in the present clay interlayers. The quantum efficiency for type II reactions of the ketocarboxylates coadsorbed with various other aliphatic and aromatic carboxylates was improved in all cases, especially for ω-(p-tolyl)hexanoate and p-(n-octyl)benzoate where two- or three-fold enhancement was observed compared to the case without coadsorption. This is rationalized on the basis of the fact that such bulky coadsorbate molecules should interfere with the rigid alignment of the substrate ketones, hence enhancing forward sequences from the 1,4-diradicals.

Finally, a heavier atom effect was examined by the addition of inorganic guest ions to the interlayer. Although a series of halogen atoms, i.e. F, Cl, Br, and I, were introduced into the interlayer under the conditions of 29–59% degree of adsorption, the type II quantum efficiency was little affected.

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