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Regioselective Photocyclodimerization of Cyclohexenones Intercalated on Clay Layers(1)

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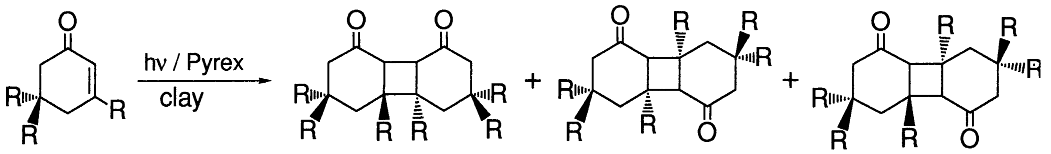
UV light irradiation of 2-cyclohexenones (**1**) in the presence of saponite clay resulted in a regioselective photodimerization affording *anti*-head-to-head dimer. The directed intercalation of **1** was suggested by the regioselective dimerization, X-ray diffraction, IR and photoluminesence analyses.

We have reported that ionic olefins such as stilbazolium ions were quantitatively intercalated on clay interlayers and gave, on irradiation, stereoselective cyclodimers, reflecting their oriented intercalation.(2) In order to utilize clay interlayers as reaction fields more generally, we undertook the photoreaction of non-ionic substrates, e.g. ketones and nitriles.

2-Cyclohexen-1-one (**1a**) was intercalated on clay interlayers by stirring with saponite clay powder in cyclohexane or benzene. It took rather longer period of *ca.*1 h in order to achieve the adsorption equilibrium at ambient temperature (around 20 °C) where 36% of added **1a** was intercalated in the clay interlayer. A suspension solution of **1a**-intercalated saponite clay in benzene was irradiated by a 300 W medium pressure Hg lamp through a Pyrex filter, giving *anti*-head-to-head cyclodimer (**2a**) predominantly along with a trace or small amount of *syn*- and *anti*-head-to-tail dimers (**3a** and **4a**).



1 **2** (*anti*-HH) **3** (*syn*-HT) **4** (*anti*-HT)

a, R = H ; **b**, R = CH_3

Table 1 summarizes the effect of saponite clay, in comparison with other additives, on the photodimerization of cyclic enones. The product ratio of HH- to HT-dimers from **1a** intercalated on saponite clay layers was as high as 17 (run 1). It was quite contrasted to the reaction in the bulk solution (run 8) which proceeded about only one tenth as fast as that on clay layers and afforded *anti*-HT dimer predominantly. Hydrotalcite, an anion exchange clay, could not improve the reactivity because of no intercalation of **1a**. Silica gel could adsorb **1a** molecules in the micropores, but the resulting stereoselectivity was quite low (see run 6). Activated alumina also gave low stereoselectivities. Similar results were obtained in the photodimerization of **1b** (R=CH_3). A small decrease in the stereoselectivities could be explained by the decreased intercalation probably due to the bulkiness of methyl

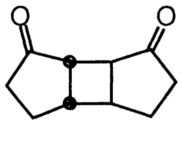
Table 1. Photodimerization of **1** and **5** under VariousConditions[a]

Run no.	Conditions[b]	Enone	Adsorption	Conversion	Selectivity[c]/%			[*anti*-HH]
			%	%	*anti*-HH	*syn*-HT	*anti*-HT	([*syn*-HT] + [*anti*-HT])
1	Saponite	**1a**	36	72	82	< 0.1	5	17
2		**1b**	26	31	62	1	6	9.4
3		**5**	48	37	11	< 0.1	8	1.4
4	Hydrotalcite[d]	**1a**	<1	40	10	< 0.1	12	0.79
5		**1b**	<1	2	41	7	21	1.5
6	Silica[e]	**1a**	36	82	20	< 0.1	18	1.1
7	Alumina[f]	**1a**	1	49	12	< 0.1	12	1.0
8	None[g]	**1a**		25	8	< 0.1	29	0.27
9		**1b**		62	1	2	2	0.26
10		**5**		46	1	< 0.1	19	0.06

a) Irradiation of 50 mM enone in benzene for 10 h with a 300 W Hg lamp through a Pyrex filter. b) Powdered clay or additives (500 mg) were dispersed in the solution of 50 mM enones in benzene (10ml) c) Product distribution based on consumed starting enones. d) Synthetic hydrotalcite (Alcamac, Kyowa Chemical Ind.). e) Wakogel Q-63, Wako Pure Chemicals. f) Activated alumina, Wako Pure Chemicals. g) Control reaction of 50 mM enone in benzene.

groups. Saponite clay showed a significant effect on the formation of *anti*-HH dimer (**6**) in the photodimerization of 2-cyclopenten-1-one (**5**), but the resulting total yields of dimers were quite low; glc analysis, employing a fused silica capillary column, showed no peaks other than **5**, **6**, and **7**. The considerable amount of *anti*-HTdimer (**7**) is presumably formed by the dimerization in the bulk solution (see run 10), since about half of added **5** is dissolved in the bulk.

It is now apparent that saponite clay accelerates the photodimerization of cyclohexenones and the regiochemistry is completely opposite to the case in bulk benzene solutions. It is reported that polar solvents favor the formation of HH dimers over HT dimers.[3] The present high selectivity for HH dimers might be partly, but not wholly, due to the polarity of the clay interlayer. This is because the polar surface of SiO_2 adsorbed the enone but was ineffective for the selective photodimerization. Thus, the interlayer surfaces of cation-exchange clays are indispensible to the present HH-selective photodimerization of enones. It is known that ketones and nitriles could be intercalated by coordinating to the cations of clay interlayers[4] and they are arranged in an ordered form much more than those on silica gel[5] or Vycor glass surfaces.[6] In homogeneous solutions, cuprous ions have been suggested to quench effectively the cyclodimer formation owing to HH type coordination with **1a**, hence the resulting HH-dimer selectivity was much lower.[7] These consideration leads to a suggestion that the present highly selective formation of HH-dimer reflects a parallel oriented adsorption of cyclohexenones toward cationic sodium ions in the clay interlayers.



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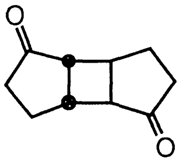

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Table 2. Clearance Space of Enone-intercalated Saponite Clays a)

Enone	Added enone / clay	Clearance space / Å	Molecular length / Å b)
1a	4.1	7.2	4.7
1b	4.3	6.5	4.7
5	4.7	6.4	4.2
None	—	5.6	—

a) Intercalation was carried out by stirring the clay suspension for 2 h. b) Calculated molecular length of the enones along the C=O axis according to the molecular models.

There is no significant difference of intercalation degrees between **1a** and **1b**. Methyl substituents exert little effect on the predominant formation of HH over HT dimers in case of saponite clay-intercalated **1**. Hence, intercalation of the enones in the clay is assumed not to be organized so tightly as to differentiate bulkiness of methyl substituents. It is surely established that the enones to be intercalated enlarge the layer space of the clay, driving out coordinated water molecules, judging from the X-ray diffraction analyses as shown in Table 2. The intercalation is such that **1a** molecules are adsorbed in a slightly inclined parallel fashion. The clearance space of **1b**- or **5**-intercalated clays was a little shorter than that expected from a doubly packed layers of enones, suggesting a more inclined adsorption. Rather small clearance spaces of enone-intercalated clays compared to enone doubly packed layer space of the clay suggest that the guest molecules would be oriented toward the interlayer-sodium cation but not in a parallel orientation almost perpendicular to the layer surfaces as observed in cases of ionic olefins such as stilbazolium ions. FT-IR spectra of **1a** intercalated on clay show that stretching vibration shifts to lower wave-number by about 25 cm^{-1} compared to neat samples, implying a coordination of carbonyl oxygen with sodium ions. On the basis of nearly 1.5 equivalents of **1a** based on CEC (cation exchange capacity) of the clay as maximum

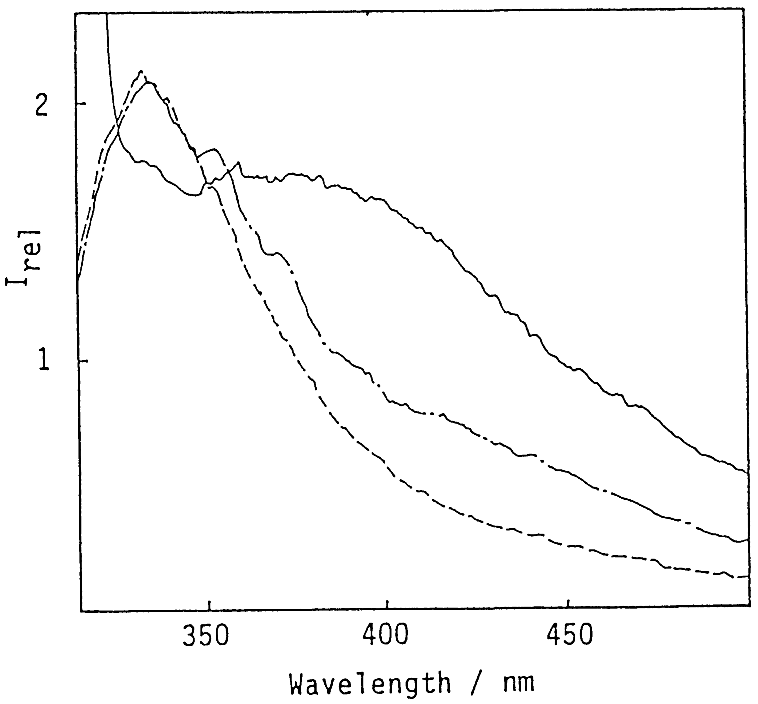

Fig. 1. Effect of saponite clay on the fluorescence spectra of **1a** in 10% aqueous methanol. Excitation: 285 nm. Concentrations:[**1a**] = 0.1 mM; [clay] = (a) 0 mM(------); (b) 0.5 mM(—•—); (c) 1.0 mM(——). Excitation: 285 nm. The spectrum (c) was scattered by clay particles below 300 nm.

amounts of intercalation, more than two enone molecules are capable to be coordinated to one sodium ion which would result in the formation of HH typed dimers. In fact, **1b** is known to coordinate to cuprous ion forming a parallel orientation.7) It is known that the dipole moment and the molecular size of intercalants affect the intercalation and the packing on clay layers.4) The present observation of selective formation of HH dimers clearly suggests that cyclohexenones are intercalated in a parallel fashion.

Figure 1 shows that **1a** exhibits fluorescence maximum at around 330 nm in 10% aqueous methanol. Addition of clay to the above solution gave new emission at around 380-500 nm in addition to the original monomer fluorescence. On increasing the amounts of saponite clay, the monomer fluorescence of **1a** was decreased and at the same time the new emission increased, which is tentatively proposed as an excimer fluorescence of **1a**. These results are rationalized by an assumption that saponite clay adsorbs the enones to make organized molecular aggregates in the interlayers. An effect of coadsorbed distearyldimethylammonium bromide (DSDAB), a cationic surfactant, on the excimer fluorescence of **1a** was examined. No excimer fluorescence was observed at all on addition of 80% intercalation of DSDAB. This fact suggest that the emission at 380 nm is surely the excimer fluorescence of **1a**. In conclusion, the present results show that clays are reaction fields controlling orientation of non-ionic but polar substrates.

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