

Spatially Controlled Photocycloaddition of a Clay-intercalated Stilbazolium Cation

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A stilbazolium cation included in clay interlayers undergoes an efficient and regioselective photocycloaddition to afford a *syn* head-to-tail dimer with suppression of the *cis-trans* isomerization.

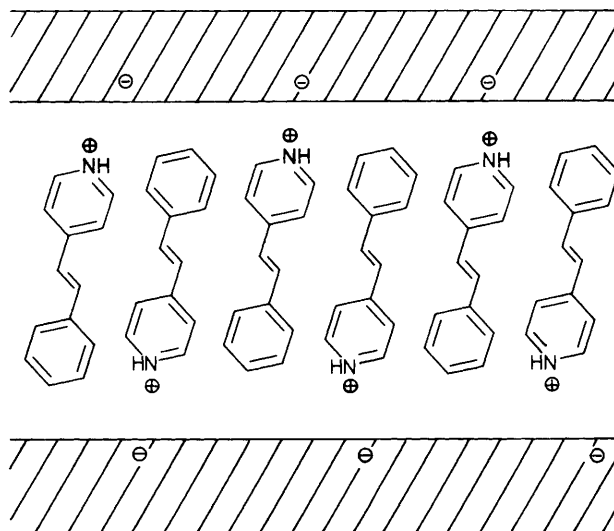
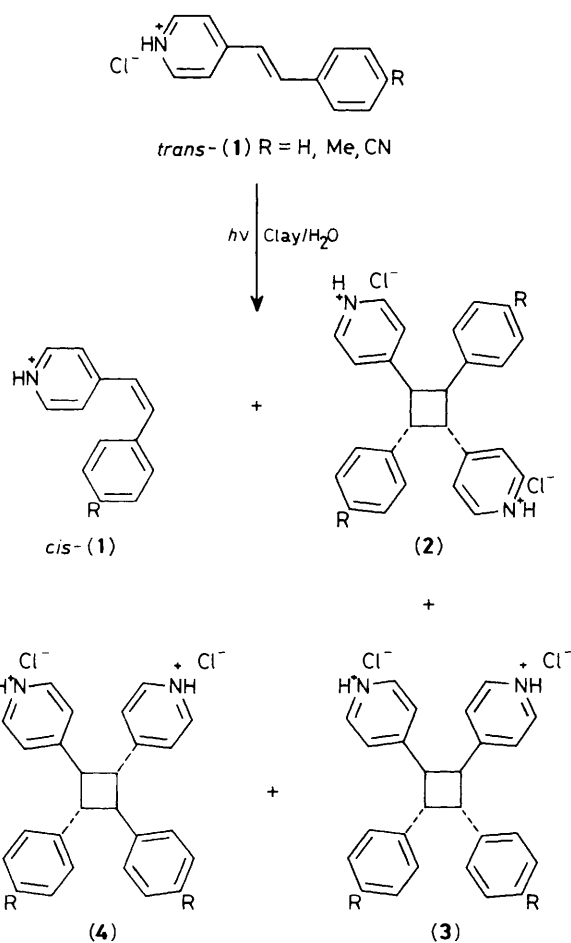
Clay minerals possess interlayer sheets with anionic sites which can intercalate some organic cations by electrostatic interaction.^{1,2,3} Only a limited number of studies, however, have been reported on the photochemical behaviour of organic molecules adsorbed on inorganic surfaces such as silica gel,⁴ zeolite,⁵ or clay minerals.⁶ These inorganic materials may provide unique reaction fields by regulating the molecular packing of adsorbed molecules.

Herein, we disclose a highly efficient photocycloaddition of a clay-intercalated stilbazolium ion (**1**) to yield predominantly a *syn* head-to-tail dimer. Intercalation of (**1**) with saponite clay was indicated by the precipitation of white solids including an equivalent amount of (**1**) on the basis of the cation exchange capacity (CEC) of the clay. A suspension of alkene (**1**)-intercalating saponite (1 mM) in water was irradiated with u.v. light through a Pyrex filter for 30 min. The photolysates were

Table 1. Effect of clay intercalation in the photolysis of *trans*-(1) in water.

R in Stilbazolium ion <i>trans</i> -(1) ^a	Reaction media	Conversion /% ^b	Photoproducts/% ^c			
			<i>cis</i> -(1)	(2)	(3)	(4)
H	H ₂ O	69	67	2	—	2
H	Clay/H ₂ O	98	14	70	5	—
Me	H ₂ O	54	59	5	—	—
Me	Clay/H ₂ O	76	14	45	—	—
CN	H ₂ O ^d	95	91	3	1	—
CN	clay/H ₂ O ^d	86	54	20	12	—

^a *trans*-(1) (1 mM) was irradiated for 30 min with and without an equivalent amount of saponite in H₂O. ^b The values are % conversions of *trans*-(1). ^c Percentages of photoproducts are based on starting *trans*-(1). ^d Irradiated in the presence of excess HCl: [HCl] = 2.4 M.

**Figure 1.** A schematic representation of the alkene packing in the interlayers of saponite clay.

the clay showed the 3.2 Å distance of the layer was extended to 6.2–6.8 Å by the intercalation of the alkene.

One likely schematic illustration of the alkene packing in the interlayers is shown in Figure 1, where alkene molecules are packed alternately in anti-parallel alignment leading to the observed preferential formation of a *syn* head-to-tail dimer.

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analysed by h.p.l.c. after the decomposition of the supporting clay by refluxing with 1 M HCl. The results are summarized in Table 1. There was no significant difference in product distributions before or after the workup.

The cyclodimerization takes place predominantly; *i.e.*, the formation of the *syn* head-to-tail dimer (2) was preferred over the *syn*-(3) and/or *anti*-head-to-head dimers (4). Another observation was the sharp decrease in the *cis*-*trans* isomerization in comparison to the homogeneous photolysis. These dramatic changes in the photochemical behaviour may be rationalized by the restricted molecular packing of (1) in the clay interlayers. Intercalation of (1) with clay is surely based on an electrostatic interaction between the ionic alkene and the anionic sites of clay (CEC).⁷ In fact, the X-ray analysis of

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