

Photodimerisation of enones in a clay microenvironment

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The photodimerisation of 2-cyclohexenone, 2-cyclopentenone and their 3-methyl derivatives is studied in the confined environment of clay interlayers. In the photolysis of 2-cyclohexenone, a remarkable regioselectivity is observed in favour of the head-to-head dimer when carried out in cation-exchanged bentonite clays while the dimerisation of 2-cyclopentenone favours the formation of the head-to-tail dimer. The results are explained on the basis of the ground state pre-organisation of enones and also the complexing ability of charge-balancing cations with the carbonyl oxygen of enone. In addition to the observed regioselectivity, other advantages of employing clays in photochemical studies are highlighted.

Introduction

Regio- and stereoselective photodimerisation reactions are of great interest due to their synthetic utility and mechanistic features.¹ In recent years selectivity has been achieved to a greater extent using constrained media.² Among the well known organised assemblies, zeolites (which are aluminosilicates having well-defined pores and channels) are widely used in photochemical reactions and photophysical studies.³ On the other hand, clays, which are ubiquitous lamellar aluminosilicates (Fig. 1), while commonly used⁴ for selective trans-

major dimers, *cis-anti-cis* head-to-tail (HT) (3) and head-to-head (HH) (4) and two minor products, (5) and (6) (Table 1). Among the two minor products, (5) is found to be a *trans*-fused HH dimer and (6) as a *cis-syn-cis* HH or *cis-syn-cis* HT dimer (Scheme 1). The reaction in non-polar solvents gives HT dimer

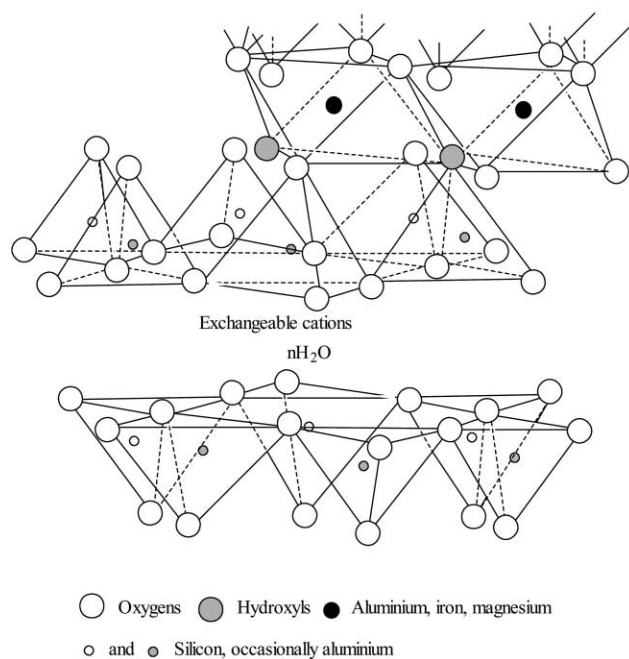
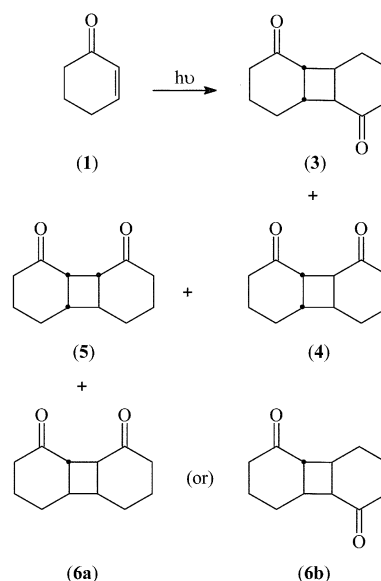


Fig. 1 Layered structure of a montmorillonite clay.

formations in thermal reactions, do not find favour from photochemists and only limited reports⁵⁻⁷ appear in the literature, despite their well-known ability as catalytic materials.⁸

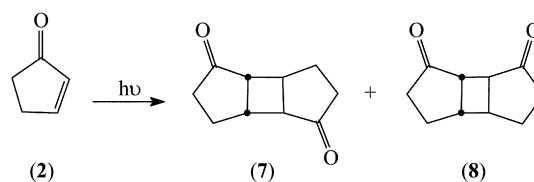
The photochemical dimerisation of enones, namely 2-cyclohexenone⁹ (1) and 2-cyclopentenone¹⁰ (2), has been studied in homogeneous media. The photodimerization of 2-cyclohexenone (1) in solution results in (through the triplet state) two



Scheme 1

as the major product and the regioselectivity switches over to HH dimer in polar solvents.^{9,11}

In the case of 2-cyclopentenone (2), head-to-tail (HT) (7) and head-to-head (HH) (8) dimers are formed from interaction between an excited triplet state molecule and a ground state one. In both polar and non-polar solvents, the major dimer formed is HT (7) (Scheme 2, Table 2).^{10,11}



Scheme 2

Table 1 Product distribution in clay-mediated photodimerisation of 2-cyclohexenone^{a,b}

Medium	% Conversion	HT (3) ^c	HH (4) ^c	(5 + 6) ^c	(5 + 6)/(3 + 4 + 5 + 6)	HT/HH ratio
Hexane	46.5	49.1	30.0	20.9	0.21	1.63
Benzene	20.4	44.4	32.2	23.4	0.23 (0.26) ^d	1.38 (1.95) ^d
Methanol	31.4	33.1	40.3	26.6	0.26 (0.14) ^d	0.82 (0.63) ^d
Saponite ^e	72.0	5.00	82.0	—	—	0.06
Li ⁺ -bentonite ^f	19.1	27.9	58.8	13.3	0.13	0.47
Na ⁺ -bentonite	30.0	25.0	59.8	15.2	0.15	0.42
K ⁺ -bentonite	17.7	24.8	61.4	13.8	0.14	0.40
Cs ⁺ -bentonite	23.1	20.8	64.2	15.0	0.15	0.32
Tl ⁺ -bentonite	6.2	17.9	70.9	11.2	0.11	0.25
Mg ²⁺ -bentonite	19.9	32.9	60.6	6.5	0.06	0.54
Ca ²⁺ -bentonite	17.8	25.3	72.8	1.9	0.02	0.35
Sr ²⁺ -bentonite	6.6	17.4	77.6	5.0	0.05	0.22
Ba ²⁺ -bentonite	3.6	17.1	77.8	5.1	0.05	0.22
Al ³⁺ -bentonite	7.7	15.6	78.9	5.5	0.05	0.19
Hydrotalcite ^e	40.0	12.0	10.0	—	—	1.20
HTlc (5 : 1)	17.4	29.6	48.9	21.5	0.21	0.60
HTlc (3 : 1)	14.8	40.5	32.9	26.1	0.26	1.23
MgY	18.7	26.4	64.4	9.2	0.09	0.41
CaY	40.7	22.9	65.3	11.8	0.12	0.35
SrY	50.1	20.5	67.3	12.2	0.12	0.30
BaY	26.5	14.9	81.4	3.7	0.04	0.18

^a Irradiations were carried out in hexane slurry under inert atmosphere and the products were extracted with dichloromethane. The mass balance was found to be about 95 %. The solution reactions were carried out in at enone concentration of 1 M. ^b Analysed by GC; Error limit \pm 2%.

^c For structure of dimers, refer to Scheme 1. ^d Data in parentheses are taken from ref. 11. ^e Data from ref. 18 ^f Li⁺-exchanged bentonite clay.

Table 2 Product distribution in clay-mediated photodimerisation of 2-cyclopentenone^{a,b}

Medium	% Conversion	HT (7) ^c	HH (8) ^c	HT/HH ratio
Benzene	36.0	73.5	26.5	2.8 (3.64) ^d
Methanol	22.0	60.9	39.1	1.6 (1.66) ^d
Hexane	84.5	74.9	25.1	2.9
Saponite ^e	37.0	8.00	11.0	0.73
Li ⁺ -bentonite ^f	27.8	87.3	12.7	6.8
Na ⁺ -bentonite	11.5	82.8	17.2	4.8
K ⁺ -bentonite	22.8	84.8	15.2	5.6
Cs ⁺ -bentonite	20.9	80.6	19.4	4.2
Tl ⁺ -bentonite	19.6	74.6	25.4	2.9
Mg ²⁺ -bentonite	28.5	87.1	12.9	6.7
Ca ²⁺ -bentonite	22.2	77.7	22.3	3.5
Sr ²⁺ -bentonite	38.0	80.1	19.9	4.2
Ba ²⁺ -bentonite	18.5	71.9	28.1	2.5
Al ³⁺ -bentonite	18.8	81.9	18.1	4.5
HTlc (5 : 1)	38.3	92.2	8.00	11.5
HTlc (3 : 1)	44.9	>98.0	—	—
SrY	19.7	56.3	43.7	1.28
BaY	50.7	43.6	56.4	0.77

^a The irradiation were carried out in hexane slurry under inert atmosphere and the products were extracted with dichloromethane. The mass balances were found to be about 95 %. The solution reactions were carried out in an enone concentration of 1 M. ^b Analysed by GC; Error limit \pm 2%.

^c For structure of dimers, refer to Scheme 2. ^d Data in parentheses are taken from ref. 11. ^e Data from ref. 18 ^f Li⁺-exchanged bentonite clay.

A survey of recent literature reveals a few [2 + 2] photocycloaddition reactions with enones such as addition of alkenes,¹² alkynes¹³ and fullerenes¹⁴ and in the acid-catalysed photoaddition of methanol to 3-alkyl-2-cyclohexenones.¹⁵

Clays have been successfully utilised in regioselective photocycloaddition of stilbazolium cations¹⁶ and for photooxidation studies.¹⁷ In the presence of saponite clays,¹⁸ irradiation of 2-cyclohexenones has resulted in regioselective photodimerization yielding the *anti*-HH dimer. However, silica and alumina (which also contain polar surfaces) are ineffective for selective photodimerization. A parallel oriented adsorption of cyclohexenones towards the sodium ion in the clay interlayer is

postulated.¹⁸ This necessitates a detailed systematic investigation on the role of clay interlayer and the charge-balancing cation on the photodimerization of enones. In a recent study¹⁹ molecular alignment (leading to bilayer formation) of 4'-chloro-4-stilbenecarboxylic acid in hydrotalcite clays has been observed, resulting in stereoselective photodimerisation.

When the photodimerisation of enones is carried out in solution, there is poor control over the regioselectivity. However, a relatively high degree of selectivity can be attained in zeolites due to the size constriction effects in the supercages and complexing ability of the charge-balancing cations.¹¹ With both 2-cyclohexenone and 2-cyclopentenone, an increase in the

formation of the HH relative to the HT dimer is observed in both X- and Y-type faujasites as the size of the counterion increases and the available space in the zeolite cavity decreases. However, in the two dimensional interlayer region of clays, the effect of size constriction will be less as the molecules move more freely and hence the effect of charge-balancing cations is expected to be the major factor in determining the regioselectivity in photodimerisation. This prompted us to study photodimerisation of enones in a clay microenvironment and the results are presented here. Control experiments show that both 2-cyclohexenone and 2-cyclopentenone are stable thermally in a clay microenvironment.

Results and discussion

In the photodimerisation of 2-cyclohexenone carried out in clays, a substantial difference in product distribution is observed compared to that obtained in hexane solution. Hexane is chosen as the solvent of choice for slurry irradiation as this would maximize the cation–enone interaction and would minimize the swelling of the clay. The formation of the HH dimer is more favoured in clays, in contrast to solution photolysis. Similar selective photodimerisation was also previously reported¹⁸ in saponite clays (Table 1). In addition, the amount of the two *trans*-fused dimers (**5**) and (**6**) (Table 1) decreases in clays. The reaction was also carried out in various monovalent as well as divalent cation-exchanged clays and zeolites and similar results were observed. A decrease in cation size causes an increase in HT dimer (comparable to those reported for zeolites¹¹) with a consequent increase in HT/HH ratio also. The trend is the same in divalent cation-exchanged clays and zeolites also. It is also interesting to observe that the ratio of (**5** + **6**)/(**3** + **4** + **5** + **6**) in clays is much smaller than that in the corresponding zeolite mediated reaction. Anionic hydrotalcite-like clays (HTlc) are also employed and the product distribution here is not much different from solution photolysis indicating that the interaction between the enone and HTlc layer is minimal. Usami *et al.*¹⁸ have also reported that hydrotalcite does not improve the reactivity and selectivity as there is no intercalation of **1**.

These observations can be explained on the basis of the complexing ability of the charge-balancing cations with the carbonyl oxygen, which tends to hold the initially aligned enone molecules in a head-to-head fashion in the interlayer, resulting in an improved yield of the HH dimer.

It is also likely that complexation between the interlayer cation and the carbonyl oxygen may result in polarisation of the carbon–carbon double bond. The smaller the cation and also the higher its charge, the stronger will be the binding. This results in an increase in polarisation of the C=C double bond, which tends to keep the molecules apart from the head-to-head orientation and hence favours the formation of the HT dimer (Fig. 2).

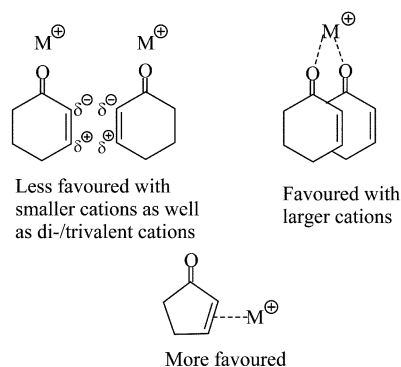


Fig. 2

Table 3 IR spectral data of enones in enone–clay complexes

Medium	$\nu_{\text{C=O}}/\text{cm}^{-1}$	
	2-Cyclohexenone	2-Cyclopentenone
CCl ₄	1692	1712
Li ⁺ –bentonite	1673	1705
Na ⁺ –bentonite	1682	1701
K ⁺ –bentonite	1681	1698
Mg ²⁺ –bentonite	1664	1702
Ca ²⁺ –bentonite	1660	1702
Al ³⁺ –bentonite	1656	1702

This effect explains the increase in the amount of HH dimer formed as the size of the charge-balancing cation increases. With larger cations, complexation with two enones is also likely (Fig. 2) which can lead to improved HH dimer formation. This is also supported by studies in anionic hydrotalcite (HTlc) clays possessing positively charged layers in their structure, wherein an overall reduction in selectivity and in the conversion of 2-cyclohexenone is observed.

Supporting evidence for cation–enone interaction in 2-cyclohexenone was obtained from IR studies. The carbon–oxygen double bond in the enone is the one which is very significantly altered upon complexation with cations. A pronounced decrease in $\nu_{\text{C=O}}$ is observed which is more pronounced with smaller cations as well as di-/trivalent cations (Table 3). It is relevant to note here that cation binding has been reported to control the reactive states in the photochemistry of enones inside zeolites.²⁰ Computational evidence (by calculating excited state energies estimated at the CIS(D)/6-31 + G* level) is presented in which Li⁺ complexation, in fact, leads to a reversal of triplet state ordering in enones. In both cyclohexenone and cyclopentenone, the lowest triplet has switched from $n \rightarrow \pi^*$ in character to $\pi \rightarrow \pi^*$ upon coordination with Li⁺. In this context, it is pertinent to note that the nature of the lowest energy triplet has been the subject of controversy for a long time. The two states (n, π^*) and (π, π^*) are very close in energy,²¹ specifically in rigid enones. Very small changes in structure and medium can alter the relative ordering of these states upon cation binding, and the (π, π^*) state in this case could be of lowest energy now.

When the clay-mediated dimerisation is extended to 2-cyclopentenone, it is surprising to note the predominant formation of the HT dimer (Table 2), unlike 2-cyclohexenone photodimerisation. This striking difference is in contrast to zeolite-mediated photodimerisation [where the HH dimer is the major product with 2-cyclohexenone (**1**) and both HT and HH are obtained in comparable yields with 2-cyclopentenone (**2**)] as the HT/HH ratio is 0.26 and 0.93 respectively in LiX. However the HT dimer is the major product with LiY and NaY (HT/HH ratio is 1.36 and 1.21 respectively). This difference in reactivity between (**1**) and (**2**) is manifested in a more remarkable manner in montmorillonite clay-mediated reaction. It is relevant to note that in saponite clays (trioctahedral layer type), irradiation of 2-cyclopentenone¹⁸ has resulted in mainly HH dimer, analogous to 2-cyclohexenone. However, a very significant decrease in percentage conversion and selectivity (HT/HH ratio) was also observed (Table 2).

Reactions carried out in solution and in clays with larger cations exhibit similar reactivity, and HT dimer is the major product. However, a decrease in cation size causes a drop in the yield of the HH dimer and the HT/HH ratio now increases, in contrast to the corresponding reaction with 2-cyclohexenone (**1**). This, we believe, may be due to a shift of binding between the metal ion and the enone. In 2-cyclopentenone (**2**), as the greater s-character of the carbonyl carbon holds the non-bonding electrons of oxygen more tightly than that of 2-cyclohexenone (**1**), a cation– π interaction (involving a C=C bond) as shown in Fig. 2 may be visualised. IR data presented in Table 3

provides support for this proposal. A closer look at Table 3 shows that while $\nu_{C=O}$ is influenced very significantly with the change of cations in 2-cyclohexenone, the effect is much less pronounced in 2-cyclopentenone.

This binding is stronger with smaller cations and is weaker or absent with an increase in cation size. Support for this assumption can be obtained from the IR data presented in Table 3. While a decrease in carbonyl stretching frequency upon cation binding is strong and progressive with an increase in cationic charge in 2-cyclohexenone (1), it is less pronounced in 2-cyclopentenone (2). It is relevant to note here that cation- π interaction plays²² a significant role in controlling selective geometric photoisomerisation of diphenylcyclopropane²³ and in promoting aggregation of aromatic molecules²⁴ and also energy transfer within Y-type zeolites.

These interesting observations have prompted us to extend the studies to 3-methyl substituted enones. However, no significant photodimerisation is observed in these cases indicating that steric constraints on the orientation of the enones in the interlayer may now be significant. However, it is relevant to note that Usami *et al.*¹⁸ have reported photodimerization of an alkylated enone, namely isophorone in saponite clays (with decreased percentage conversion and selectivity).

Conclusions

The results of the present study on photodimerisation amply demonstrate that layered aluminosilicate clays can also be used as versatile media for stereoselective photodimerisation reactions of enones. With lesser hindrance to mobility inside clay interlayers, the ground state pre-organisation of enones and the interaction between charge-balancing cations and enones play a more significant role in controlling the distribution of products while the regiochemistry of dimer formation is normally influenced by the differential decay of intermediate diradicals.²⁵ The study thus throws valuable insight into cation-enone interaction in an organised media.

Experimental

Materials

2-Cyclohexenone and 3-methyl-2-cyclopentenone were obtained from E. Merck. 2-Cyclopentenone, bentonite clay and NaY zeolite were supplied by Aldrich. 3-Methyl-2-cyclohexenone was prepared from ethyl acetoacetate and *para*-formaldehyde as in the reported procedure.²⁶ All the solvents used were of HPLC grade and used without further purification.

Preparation of cation-exchanged clays^{4a,27} and zeolites.²⁸ Bentonite clay (5 g) and 125 mL of respective metal nitrate solution (1 M) were stirred at room temperature for three days. It was then filtered, washed well with deionised water and dried at 110 °C for 8 h. The divalent cation of interest were exchanged into the zeolite, NaY powder (5 g) by stirring with the corresponding nitrate (50 mL, 10%) solution at 90 °C for about 12 h. The exchange was repeated at least three times. Each time after exchange, the zeolite powder was washed repeatedly with distilled water and then dried. The zeolites were activated at 450 °C for 6 h prior to use.

Preparation of hydrotalcites (HTlc). Various hydrotalcites were prepared by the literature procedure²⁹ and a typical example for 5 : 1 HTlc is reported below: $Al(NO_3)_3 \cdot 9H_2O$ (0.01 mol) and $Mg(NO_3)_2 \cdot 6H_2O$ (0.05 mol) were dissolved in deionised water (100 mL), and a second solution (60 mL) of Na_2CO_3 (0.03 mol) and NaOH (0.07 mol) was prepared. After the first solution was slowly added to the second one, the resulting mixture was heated at 65 °C for 18 h with vigorous stirring. The

white slurry was then cooled to room temperature, filtered, washed well with deionised water and dried overnight at 110 °C. They were characterised by TGA-DTA analysis (Netzsch STA 409PC instrument) which showed two endothermic transitions. The first transition at lower temperature (149 °C) was corresponding to the loss of interlayer water and the second one at high temperature (413 °C) to the loss of hydroxyl groups and carbonates decomposition as reported earlier.²⁹

Photolysis. In a typical photolysis experiment, 50 mg of the enone and 200 mg of the cation-exchanged clay were irradiated as a hexane slurry (5 mL) in a 365 nm multilamp reactor for 8 h under nitrogen atmosphere. Control experiments show that not only are the enones thermally stable under the present conditions, but they also are found to be absent from the hexane solvent indicating that all the enones are adsorbed on clay. After irradiation, the products were extracted with 25 mL of dichloromethane, concentrated under reduced pressure and analysed by GC (Shimadzu GC-17A, SE 30(10%) capillary column, FID detector and high purity nitrogen as the carrier gas).

In a zeolite-mediated reaction, 200 mg of the zeolite (pre-heated to 450 °C for 6 h) and 10 mg of the enone (Loading is 5% by weight)¹¹ were irradiated as a hexane slurry as described above. After treatment with 1M HCl (1mL), the products are extracted with dichloromethane (25 mL), concentrated under reduced pressure and analysed by GC.

The products were identified by their characteristic mass spectral pattern (Finnigan GC-MS, RTX5-MS column, high purity helium as the carrier gas) and also by comparison with authentic samples. Solution irradiations were carried out with 1 M solutions under identical conditions.

Characterisation of clay-enone complexes. 200 mg of the cation-exchanged bentonite and 50 mg of enone were stirred well as hexane slurry (5 mL) for 3 h and the solvent was evaporated under vacuum. The IR spectra of the clay-enone complexes thus obtained are recorded as KBr pellets utilizing a JASCO FT-IR 410 spectrometer.

Acknowledgements

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