

## Interaction of Smectites with Organic Photochromic Compounds

J. M. ADAMS\* and A. J. GABBUTT

*Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, Dyfed, SY23 1NE.*

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**Abstract.** Reversible light induced colour changes have been observed in a variety of organic and inorganic systems: the phenomenon is termed photochromism. Suitable materials have potential uses ranging from data storage to labelling. The fulgide  $\alpha$ -2,5-dimethyl-3-furylethylidene (isopropylidene) succinic anhydride shows photochromic behaviour which is modified considerably when the fulgide is supported on a smectite clay. We have shown that smectites cause a bathochromic shift in the light absorption of the fulgide and the photochrome of 20 and 80 nm, respectively, relative to the values in hydrocarbon solution. Moreover, the clays catalyse several reactions on different timescales.

- (1)  $Z \rightarrow E$  isomerization of the fulgide. This process is an acid catalysed interlayer reaction strongly sensitive to the presence of polar molecules even at low concentrations. The most effective catalysts were clays exchanged with trivalent interlayer cations, equilibrated at low relative humidity before use. In toluene, reflux reactions were complete in  $\sim 1$  hour. The procedure can be used in a preparative sense.
- (2) The ring closure reaction to give the photochrome (i.e.  $E \rightarrow P$ ). This is a surface (and interlayer) catalysed thermal reaction, taking of the order of a day in toluene reflux. The reaction does not depend to any great extent on the type of smectite used, nor, within reason, on any pretreatment of the clay.
- (3) The decomposition of the fulgide and photochrome. These reactions were found to be acid catalysed and gave at least four products. The reactions occur in the interlayer region of the clay, but at a rate slower than those listed above, taking months to reach levels at which products could be detected.

Although the shifts in light absorption noted above are of potential interest in a range of applications, the chemical activity of the clay, and the resistance of the coloured form to bleaching when supported on the clay, make such usage unlikely.

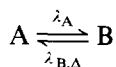
**Key words.** Clay, smectite, montmorillonite, bentonite, catalyst, isomerization, photochromism, ring closure.

### 1. Introduction

It is well known that smectite clays react with many organic species with change of colour [1, 2]. A number of these 'colour reactions' find commercial use. For example, in carbonless copy papers, colour development is due to protonation of a dye precursor such as crystal violet lactone or *N*-benzoyl leuco methylene blue by an acid activated clay to give a cationic dye [3]. While the reactivity in this case is of a Brønsted acid type, other colour reactions involve Lewis acid sites on clay edges and one-electron transfer processes. In the conversion of benzidine to the blue monovalent radical cation, Lewis acid and one-electron sites are involved, while conversion to the yellow divalent radical cation requires Brønsted activity [2, 4, 5].

\* Present address: ECC International Ltd., John Keay House, St. Austell, Cornwall PL25 4DJ, England.

Recently, there has been some interest in materials which change colour reversibly on exposure to light of appropriate wavelengths. The process is known as photochromism and can be represented by:



where A and B are the molecular species involved,  $\lambda_A$  and  $\lambda_B$  are the suitable wavelengths of light and  $\Delta$  represents heat.

Applications envisaged for photochromic materials can be split into two types: image and non-image forming. The former category includes photographic printing, data displays, photographic recording and optical memory [6], while photographic masking, anti-glare screens and actinometry [7] are examples of the latter.

The present study concerns a class of organic photochromic materials known as fulgides. Trundle [8] demonstrated that when certain of these compounds were sorbed on smectite clays, there was a significant shift in the wavelength of the maximum of the light absorption. Fulgides which normally produced a coloured form which was red, gave one which was blue when supported on the clay, changes which could normally only be achieved by synthesis of molecules with very different chemical substituents.

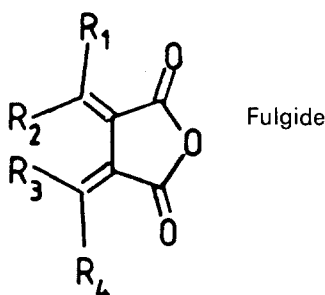
This preliminary work suggested that it might be fruitful to examine the interactions between smectite clays and fulgides.

### 1.1. FULGIDES

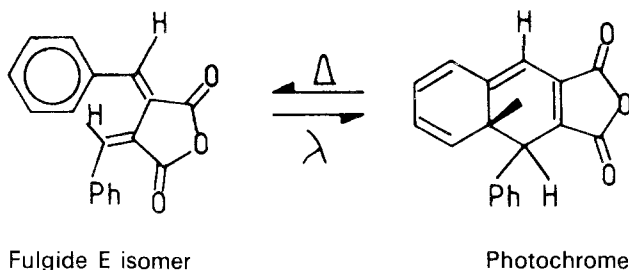
Fulgides (Scheme 1) are acid anhydrides: they were first synthesised by Stobbe [9] by cyclisation of the corresponding diacid with acetyl chloride.

Stobbe [10] found that crystals of the compounds were thermochromic (i.e. they changed color on heating), with colours which were dependent on the number of aryl substituents. Moreover, he noted that fulgides with at least one aryl substituent were photochromic, i.e. on irradiation with UV light the materials changed from yellow to red, a process which could be reversed thermally, or by exposure to white light.

In 1968, Santiago and Becker proposed [11] that the coloured species obtained from co-ordination of dibenzylidene succinic anhydride was a 1,8a dihydronaphthalene (Scheme 2).



Scheme 1.  $R_1$ — $R_4$  are alkyl or aryl substituents.



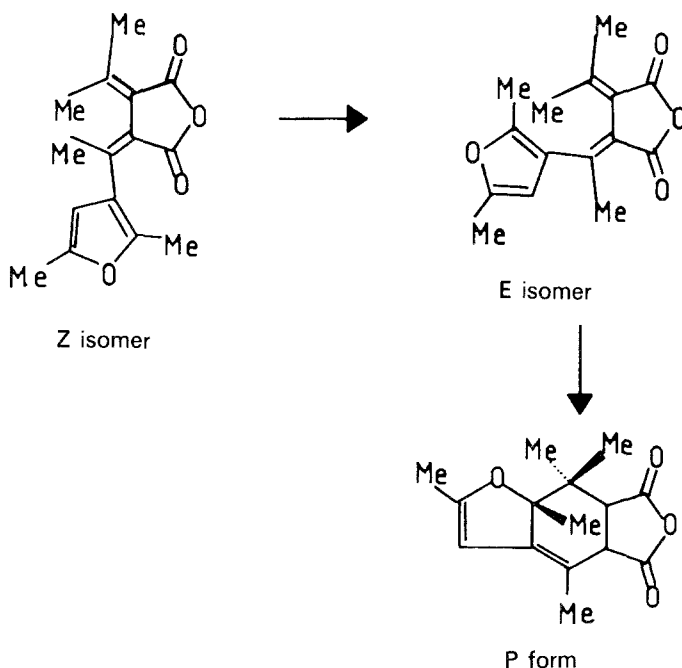
Scheme 2.

This was confirmed subsequently by Hart *et al.* [12], who proposed that the photochrome was produced by a concerted conrotatory electrocyclic ring closure in accordance with Woodward–Hoffman selection rules [13].

Considerable work has been carried out on this class of materials to obtain the particular color changes required for specific applications and to reduce fatigue, i.e. to allow many cycles (see, e.g. [14]).

The work described here was carried out using the fulgide  $\alpha$ -(2,5-dimethyl-3-furyl) ethylidene (isopropylidene) succinic anhydride. Two isomers exist, the *Z* and *E* forms, of which only the *E* isomer is converted to the *P* form on exposure to ultraviolet light (Scheme 3).

The optical absorption spectra of the *E* and *P* forms are given in Figure 1.



Scheme 3.

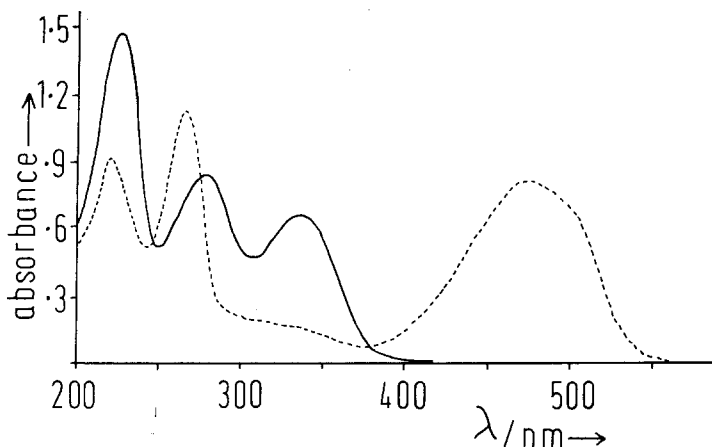


Fig. 1. UV/visible absorption spectra for the *E*-isomer (—) and the photochrome (·····). Solutions were  $10^{-4}$  mol dm $^{-3}$  in hexane. 1 cm cells were used.

## 2. Experimental

Trundle's preliminary work [8] was carried out using an unmodified Wyoming bentonite. In the present study, a variety of samples containing smectite were employed (Table I). In each case the  $<2 \mu\text{m}$  fraction was collected by sedimentation. Cation exchange of this fraction was carried out by exposing the clay to salt solutions between 0.6 and 1.0 mol dm $^{-3}$  for 24 h, after which repetitive centrifugation and washing was carried out until the excess salt had been removed.

All clay samples were dried at 80°C after which they were milled to pass through a 100 mesh screen. The water contents of the various clays were controlled by equilibration of samples (already placed in reaction vessels) over saturated salt solutions for 24 h. After removal from the equilibration chamber, reactant solution was immediately introduced over the clay (to prevent reabsorption of water from the atmosphere) and the reaction vessels were sealed.

$^1\text{H}$  nuclear magnetic resonance (NMR) spectra of the various forms of the fulgide were significantly different (Figure 2), allowing ready monitoring of experiments in

Table I. Summary of clays used

Sample	Code name
Belle Fourche Mine, S. Dakota (Wards)	MON 2
Texas (ECCI)	MON 3
Wyoming Bentonite (Hopkin & Williams)	MON 4
NWT 19 (Japanese clay, Wiggins Teape)	MON 19
NWT 20 (Japanese clay, Wiggins Teape)	MON 20
Bentonite, Polkville, Mississippi (Chisholm Mine, Wards)	MON 21
Bentonite, Amory, Mississippi (Wards)	MON 22A
Beidellite, Cameron, Arizona (Wards)	MON 31
Metabentonite, Strasbourg, Virginia (Wards)	MON 37

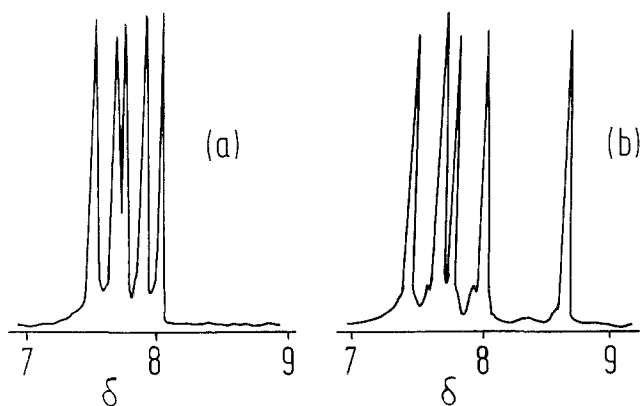


Fig. 2. NMR spectra for (a) *Z*-isomer and (b) *E*-isomer.

many cases. A modified NMR tube was used as the reaction vessel (Figure 3). After reaction, the vessel was inverted and placed in the Perkin Elmer R12 NMR spectrometer. The magnetic flea was retained in the bulb section by the constriction, while the clay settled so that it did not intrude into the sampling volume.

Optical spectra were collected by diffuse reflectance (Pye Unicam SP1700) from discs pressed at 5 ton/in<sup>2</sup> for 30 minutes. X-ray diffraction data were collected using CuK<sub>α</sub> radiation with a Philips PW1050 diffractometer.

For high performance liquid chromatography (HPLC), 100 mm columns were used, packed with Hypersil. The chromatograph itself was a Spectra-Physics 3500B machine linked to a SP8200 UV/visible detector operating at 312 nm.

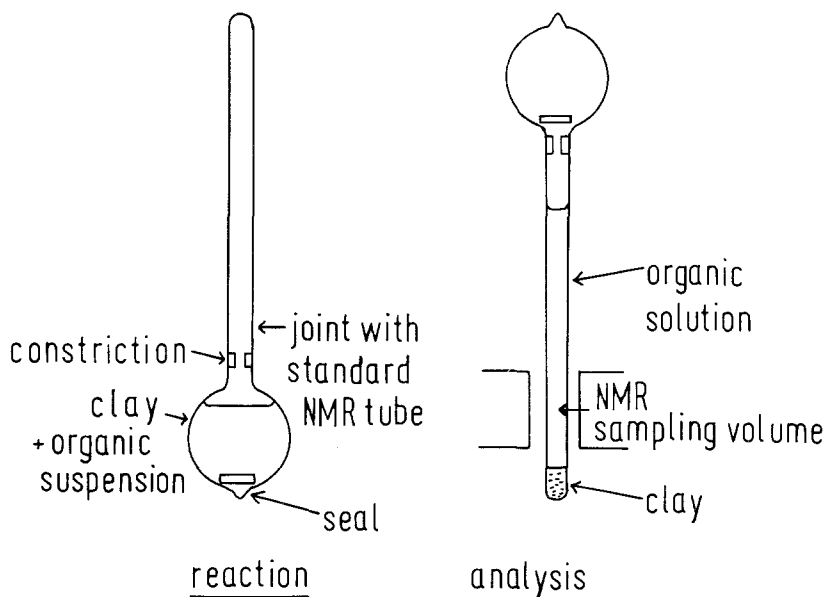


Fig. 3. Reaction vessel used in studies of *Z* → *E* isomerisation.

### 3. Results and Discussion

#### 3.1. PRELIMINARY WORK

A set of experiments was carried out in which 2 g samples of the various clays were heated under reflux with 200 mL of a 1% (w/v) solution of the fulgide (3:1 ratio of the *E*:*Z* isomers) in toluene. The clays had not been cation exchanged in any way, and were equilibrated only to ambient relative humidity. On heating, all clays became coloured to some extent, with the Wyoming clay (MON 4) in particular taking on an intense blue coloration. In addition, the organic solutions surrounding those clays which became blue took on the red coloration associated with the formation of the photochrome.

Optical spectra for samples of MON 3 (Figure 4) are typical of those for all clays. The absorption peaks at 360 nm and 540 nm were assigned to the fulgide and photochrome respectively. In comparison with the species in hexane solution (Figure 1) the peaks were shifted bathochromically by 20 and 80 nm respectively and were also broadened. This type of behaviour is consistent with the findings of Darcy [6]. He showed that an increase in the permittivity of the solvent produced bathochromic shifts for both fulgide and photochrome. Sorption on the polar clay structure appears to have caused similar behaviour.

The differences seen between clay samples were in the overall intensities of the absorbances, indicating that the clays did not take up fulgide to the same degree,

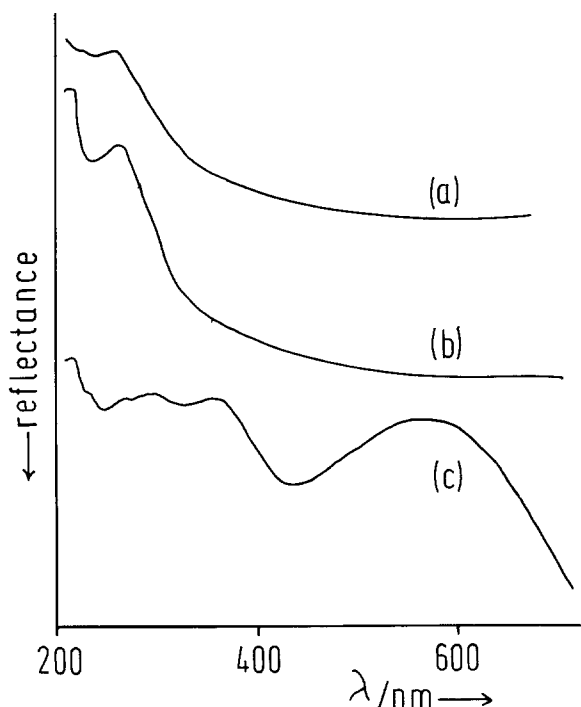


Fig. 4. UV/visible diffuse reflectance spectra of Texas montmorillonite (MON 3) (a) untreated, (b) after reflux in toluene, (c) after reflux in a 1% solution of fulgide in toluene. Note: scales displaced for clarity.

Table II. Uptake of fulgide by  $<2\ \mu\text{m}$  fraction of clay samples<sup>a</sup>

		Loadings (wt.%)	$d_{001}/\text{\AA}$
MON	2	7	13.4
MON	3	7	13.5
MON	4	10	13.1
MON	19	9	13.5
MON	20	13	13.5
MON	21	2	11.1
MON	22A	3	11.7
MON	31	2	11.7
MON	37	2	11.7

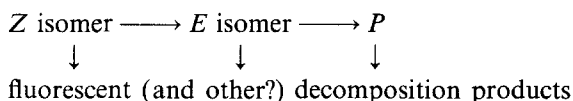
<sup>a</sup>Loadings measured by evaporating methanol washings to dryness.

and in the *relative* intensities of the 360 and 540 nm peaks, suggesting that the clays are not equally efficient at catalysing the ring closure reaction.

It appeared that the clays could be split into two groups. Group A clays showed no indication of the photochrome until they were exposed to ultraviolet light (MON 21, 22A, 31, 37), while Group B clays showed significant coloration and produced the photochrome without irradiation (MON 2, 3, 4, 19, 20). Again, Group A clays took up  $<3\%$  (w/w) of fulgide, while the figure for the Group B clays was 7% or more (Table II). Two conclusions could be drawn from this work. Firstly, the clays catalysed the ring closure of the fulgide to the photochrome by a *thermal* rather than the normal *photo* route.<sup>1</sup> Secondly, not all the clays were equally efficient as catalysts for the conversion.

Two other preliminary experiments were considered noteworthy. In the first, an attempt was being made to measure the uptake of the fulgide from solution. The pure *Z* isomer was used, since the configuration of this species is such that it cannot undergo the ring closure reaction. The uptake experiment was performed in the dark to prevent isomerization ( $Z \rightarrow E$ ) and ring closure ( $E \rightarrow P$ ) reactions taking place as a result of incident light. Despite these precautions, the solution became coloured. It was, therefore, considered that the clay was capable of catalysing not only the ring closure, but also the *Z* to *E* isomerization. In the second experiment, fulgide and photochrome were being washed from a Group B clay with methanol. On irradiation, the solutions were found to contain some fluorescent material, obviously decomposition products of the fulgide and/or the photochrome.

Overall, then, it appeared that clays could be responsible for catalysing the following interconversions:



Scheme 4.

<sup>1</sup> Even in the dark, the photochrome was produced from the fulgide.

The various interconversions were studied in more detail. Despite the apparent complexity of the system, useful data were attainable, since the various reactions (as will be seen below) occur on very different timescales.

### 3.2. Z-E ISOMERIZATION

Irradiation of the *Z* isomer with light of 366 nm wavelength is known to result in conversion to the *E* isomer, followed immediately by quantitative conversion to the photochrome [6]. Total conversion is achieved after a period of 112 hours. Bleaching of the photochrome with white light yields the *E* isomer quantitatively. It is this indirect method which is used to convert the *Z* to the *E* form. The extended period necessary for the photo conversion results from the need to use very dilute solutions to prevent internal filtering.

In the present work, the *Z* to *E* conversion was monitored by NMR spectroscopy: the environments of the methyl protons are different in the two forms (Figure 2). Moreover, NMR is sensitive to the presence of other reaction products. On the timescale of the *Z* → *E* conversions, no photochrome or other materials were detected.

The reaction vessels used (Figure 3) allowed reactions to be carried out at constant temperature by immersion of the bulb in a refluxing solvent bath. At intervals, the reaction vessel was removed from the bath, inverted and a <sup>1</sup>H NMR spectrum taken. The errors introduced by sampling were considered to be acceptable, the time necessary to obtain a spectrum being ~1 minute in a total experimental time of ~1 hour.

Plots of  $\alpha$  (the extent of reaction) vs time were easily obtained. While several kinetic formulations were tested (first order, contracting circle, Avrami-Erofeev etc.), only the equation for a 2-D diffusion controlled reaction gave a reasonable straight line fit to the data points, i.e.

$$(1 - \alpha)\ln(1 - \alpha) + \alpha = kt/r^2.$$

#### 3.2.1. Factors Affecting the Reaction Rate

In the experiments carried out below, all factors other than that under scrutiny were kept constant. Where reaction rate coefficients are quoted, they refer to  $(k/r^2)$  in the equation above. Experimental details are given in each case with the relevant figure or table.

- (i) *Weight of Clay*. It can be seen (Figure 5) that the reaction rate increased as the weight of catalyst was raised. However, the curve deviated from linearity, a result of mixing problems at the higher weights.<sup>2</sup> In later experiments, the weights of catalysts were held almost constant and rates of reactions were adjusted to 'constant weight' values by use of the calibration data in Figure 5.
- (ii) *Concentration of the Fulgide Z isomer*. Three fulgide concentrations were compared: 5, 7.5 and 10% (w/v), the upper limit being set by the solubility of

<sup>2</sup> This interpretation is consistent with the experimental fact that reaction rates were found to depend on the stirring rate which was, therefore, fixed for all the work reported here.



the organic species. The weight adjusted rates were effectively independent of the fulgide concentration (Table III).

- (iii) *Temperature.* Over the temperature range 80 to 102°C, the reaction rate doubled (Figure 6), corresponding to an activation energy of  $\sim 33 \text{ kJ mol}^{-1}$ .
- (iv) *Interlayer Water Content.* The rate of reaction was critically dependent on the water content, the highest rates being given by samples having the lowest water levels (Figure 7).
- (v) *Interlayer Cation.* Clay samples exchanged with a variety of interlayer cations gave reaction rates which varied considerably. It is clear (Figure 8) that (with

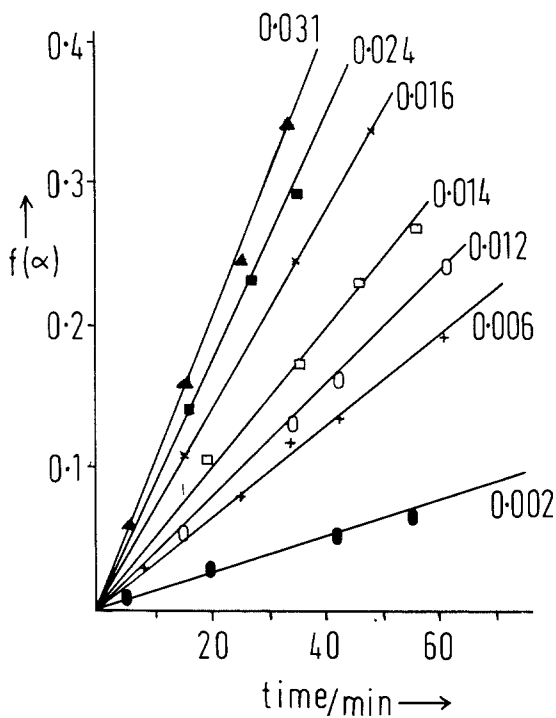


Fig. 5. Plot of  $f(\alpha)$  [i.e.  $(1 - \alpha)\ln(1 - \alpha) + \alpha$ ] vs time for isomerization reactions carried out with various weights of clay. Weights used in each case (in g) are indicated. The clay employed was MON 20, equilibrated at 15% RH before use. The reflux temperature was 88°C (benzene).

Table III. Reaction rate as a function of fulgide concentration

Fulgide concentration (% w/v)	Rate constant/min <sup>-1</sup>
5.0	$5.2 \times 10^{-3}$
7.5	$5.2 \times 10^{-3}$
10.0	$4.5 \times 10^{-3}$

Clay: MON 20 equilibrated at 15% relative humidity before use  
 Solvent: Benzene  
 Temperature: 88.5°C

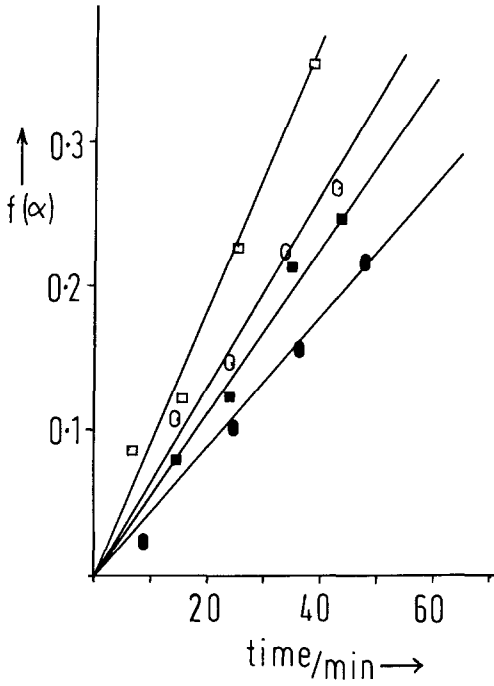


Fig. 6. Plot of  $f(\alpha)$  [i.e.  $(1-\alpha)\ln(1-\alpha) + \alpha$ ] vs time for reactions carried out at 80°C (●), 88°C (■), 95°C (○), 102°C (□). Clay used: MON 20, equilibrated at 15% RH before use. Clay weight, 0.014 g.

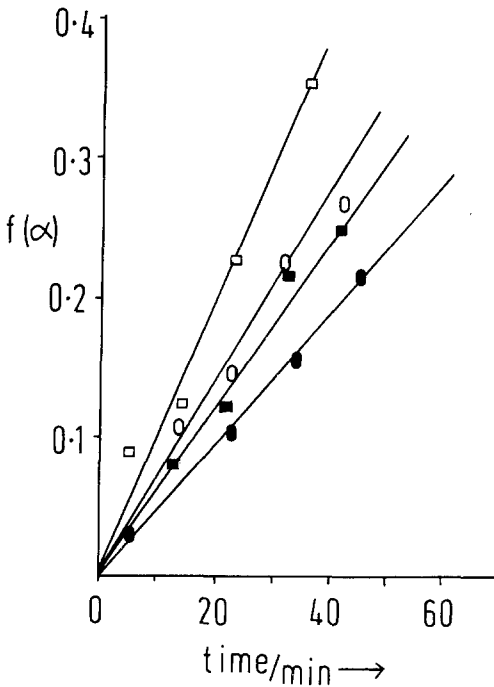


Fig. 7. Plot of  $f(\alpha)$  [i.e.  $(1-\alpha)\ln(1-\alpha) + \alpha$ ] vs time for reactions carried out with MON 20 clay equilibrated at various RH's before use: 15% RH (□), 30% RH (○), 75% RH (■), 98% RH (●).

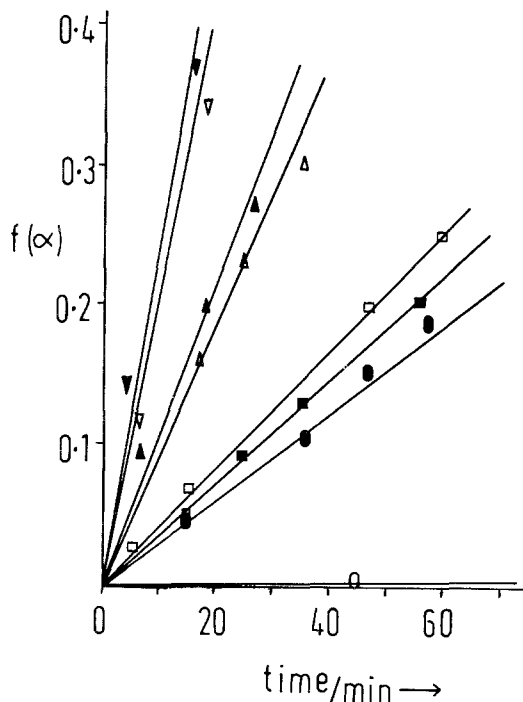


Fig. 8. Effect of variation of interlayer cation. The clay used was Wyoming bentonite (MON 4) exchanged with the following cations:  $\text{Na}^+$  ( $\circ$ ),  $\text{Ca}^{2+}$  ( $\bullet$ ),  $\text{Co}^{2+}$  ( $\blacksquare$ ),  $\text{Ni}^{2+}$  ( $\square$ ),  $\text{Cr}^{3+}$  ( $\triangle$ ),  $\text{Al}^{3+}$  ( $\blacktriangle$ ),  $\text{Cu}^{2+}$  ( $\nabla$ ),  $\text{Fe}^{3+}$  ( $\blacktriangledown$ ).

Table IV. Effect of solvent on the rate of reaction

Solvent	B. pt.	Rate constant/ $\text{min}^{-1}$
Benzene	88	$766 \times 10^{-5}$
Chloroform	61	$643 \times 10^{-5}$
1,4-dioxan	88.1	$4 \times 10^{-5}$
Acetone	56	no reaction
Ethanol	78	no reaction
Acetonitrile	81	$4 \times 10^{-5}$

Clay: MON 20 equilibrated at 15% relative humidity before use  
 Temperature: 88.5°C

the sole exception of  $\text{Cu}^{2+}$ ) the rate of reaction increased with the charge density on the exchangeable cation.

- (vi) *Solvent.* The reaction was carried out in several different solvents. It can be seen (Table IV) that when polar solvents were used, the reaction was completely suppressed. This point was addressed further by doping (deuterated) acetone into a reaction mixture made up using benzene. At  $\sim 0.3\%$  of total solvent, the addition of this polar material stopped all reaction.

## 3.2.2. Mechanism of the Reaction

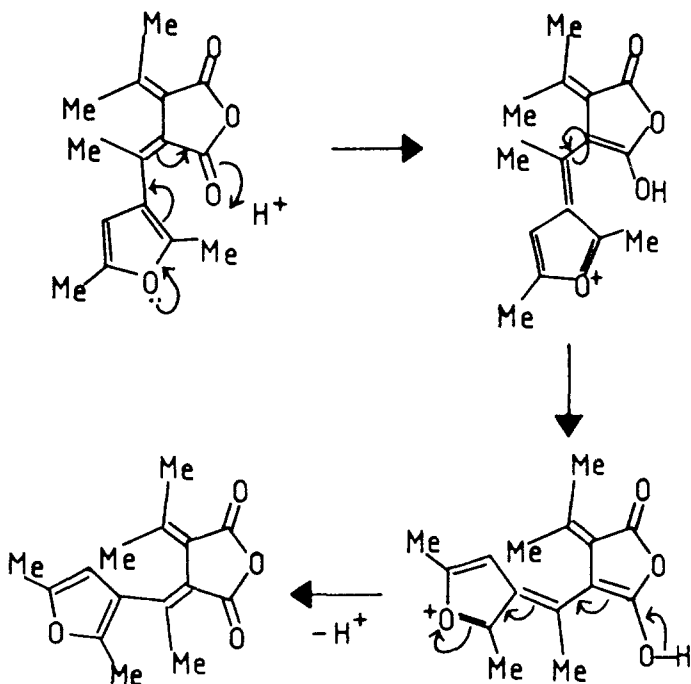
The reaction rate was found to be determined not by the fulgide concentration, but by characteristics of the clay itself. Indeed, the variation in reaction rates which resulted from use of different clay interlayer cations and water contents is typical of that seen for a multitude of Brønsted acid catalysed reactions (see, e.g. [15, 16]). The Brønsted activity derives from polarisation of interlayer water molecules, which is especially pronounced with small, highly charged, metal cations and at low water contents [17]:



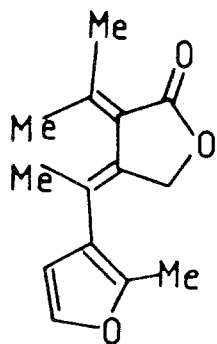
The suppression of the reaction by addition of polar solvents is most likely related to their ability to replace water in the co-ordination sphere of the interlayer cation, thereby reducing the number of 'free' protons produced. Indeed, the amount of polar solvent necessary to suppress reaction corresponds to more than that required to fill the co-ordination sphere of the interlayer cations present.

The conversion of the *Z* to the *E* isomer requires the protonation of the *Z* isomer at *one* of the anhydride oxygen atoms. This would allow rotation around what is normally a carbon-carbon double bond (Scheme 5).

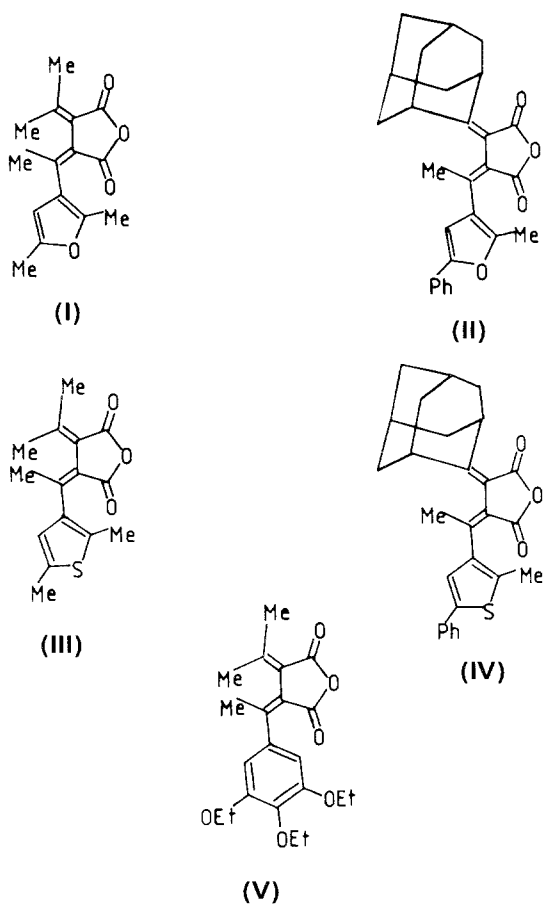
To test this scheme, an alternative fulgide was also studied. The *Z* isomer of this compound did not have an oxygen atom available for protonation and conjugated to the carbon-carbon double bond (Scheme 6).



Scheme 5.



Scheme 6.



Scheme 7.

The NMR spectrum of this fulgide showed no change over a period of over 24 hours at the temperatures normally used (88.5°C).

We conclude that this isomerization reaction is acid catalysed and that isomerization is dependent upon protonation of the carbonyl oxygen which is conjugated to the double bond, and about which rotation is necessary.

### 3.2.3. *Effect of Substitution in the Fulgide Structure*

A further series of reactions was carried out with a variety of substituted fulgides (Scheme 7).

It was found that the rate of reaction of fulgide (II) was similar to that of fulgide (I), indicating that neither substitution of the furan ring, nor the presence of bulky substituents in the 6-positions was critical, in agreement with the mechanism proposed above.

The nature of the aromatic/heterocyclic substituent does, however, produce a profound effect. Fulgides (III) and (IV) were found to react much more slowly than fulgide (I) at 88°C, comparative rates only being achieved when heated at 102°C. Fulgide (V) was also found to isomerize marginally slower than fulgide (I). These observations are consistent with the order of stability of the cationic intermediates formed during the reaction, the stability depending on the aromatic character of the aryl substituent.

### 3.3. RING CLOSURE REACTION (*E-P*)

The preliminary experiments carried out with untreated clays had shown that they could be split into two groups, A and B, the first of which took up little fulgide (<3%) and needed irradiation with UV light to produce the photochrome, and the latter, which took up >7% fulgide and converted some of it to the photochrome thermally. In this case, some of the photochrome was sorbed on the clay, while some was to be found in the supernatant solution.

It was considered that the differences between the smectites were likely to be in terms of the layer charge or the type of interlayer cation present. Some work was carried out on a range of cation exchanged clays (MON 4). After reaction, reflectance spectra showed that the absorption maximum varied only slightly in

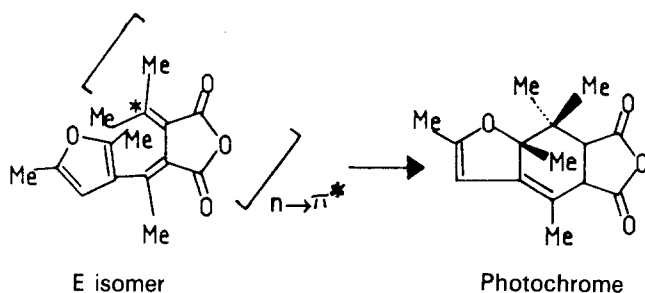
Table V. Wavelengths of absorption maxima of photochrome on different cation exchanged clays (MON 4)

Interlayer cation	nm
Na <sup>+</sup>	540
Ca <sup>2+</sup>	560
Co <sup>2+</sup>	550
Ni <sup>2+</sup>	550
Al <sup>3+</sup>	540
Cr <sup>3+</sup>	540
Fe <sup>3+</sup>	520

position (Table V), and that the differences in colour derived from the relative concentrations of fulgide and photochrome. Clays containing predominantly fulgide were red, whilst those containing predominantly photochrome were blue. Clays with substantial concentrations of both species were almost black.

The different fulgide/photochrome ratios might, in principle, be a function of the ability to catalyse the ring closure reaction, or to differences in the ability to intercalate the two species. It is, however, difficult to see why this latter possibility should occur. Both fulgide and photochrome are equally polar and of similar 'coordinating power'.

We return to the question of catalysis of the  $E \rightarrow P$  transformation. Megit [18] provided evidence that  $n \rightarrow \pi^*$  excitation of one of the carbonyl chromophores is the primary step in the photocyclisation of fulgides. Cyclisation can be thought of as an attack of the terminal carbon of the excited chromophore onto the substituted furan ring, or from the furan ring into the doubly bonded carbon, a process analogous to electrophilic attack (Scheme 8):



Scheme 8.

Such a mechanism is consistent with overcrowding in the fulgide structure, which causes the two 'halves' of the molecule to be twisted by  $\sim 30^\circ$ , preventing coplanarity ([19], Figure 9).

This photocatalysed process is concerted and follows Woodward–Hoffman rules. A thermal reaction, on the other hand, would involve disrotary rather than conrotary motion during cyclisation.<sup>3</sup> There is, however, no obvious acid-catalysed route to the product.

Examination of the data for clays containing various interlayer cations (Table VI) reinforces the view that there is no relationship between the polarising power of the interlayer cation (and hence acidity) and the amount of fulgide/photochrome taken up, or the ratio of the two species.

It is possible, however, that the reaction would be enhanced by geometrical constraints on the molecule, such as has been seen recently in Diels–Alder reactions catalysed by smectites [20]. Indeed, Glaze [21] observed catalysis of the  $E \rightarrow P$  reaction on the surface of carbon. Under reflux, the basal spacing of the clay would be dependent on the amount of water lost and of solvent and fulgide taken up in

<sup>3</sup> In the case of unsymmetrical substitution at the carbon atom, the product of the thermal and photo reactions would have different optical activity.

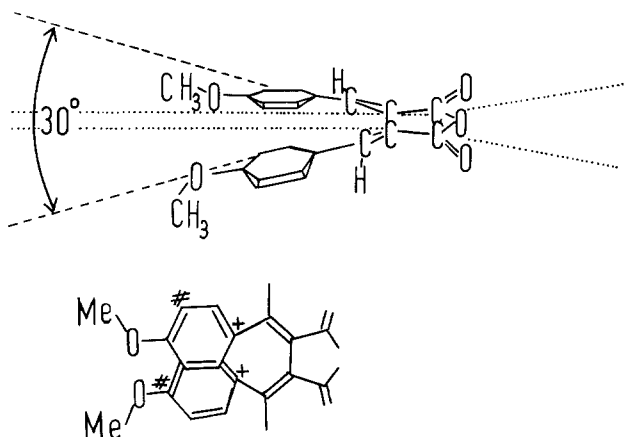


Fig. 9. Twisting of aryl substituents out of the plane of the anhydride ring in the *E*-isomer of a fulgide [19]. Atoms marked + and # are 0.26 and 0.35 Å respectively above and below the plane of the anhydride ring.

the interlayer space. On filtration and drying, some solvent would be lost and the clay layers might well constrain the fulgide molecules, encouraging the formation of the planar, photochromic, species.

It should be noted that the timescale involved in the ring closure reaction is longer than that for the *Z* → *E* conversion. The earlier experiments on the isomerization reaction showed no evidence of formation of photochrome. Moreover, in a later study, the concentrations of fulgide and photochrome were measured in the external solution after reflux in toluene solvent.<sup>4</sup> For MON 4 clays, roughly one-fifth of the fulgide was converted to photochrome after 24 hours (0.7 g clay, 200 cm<sup>3</sup> of 0.25% (w/v) solution of fulgide in toluene, reflux), a rate only about one-hundredth of that of the *Z* → *E* isomerization.

One other point of interest is that while the photochrome can normally be bleached back to fulgide by exposure to green light, that supported on Group B clays was resistant to light induced ring opening. This may be a result of steric constraints. Indeed, similar stabilisation of transition metal ethylenediamine complexes is well established [22].

Table VI. Uptake of fulgide onto various cation exchanged forms of MON 4

Interlayer cation	Loading of fulgide/ photochrome (wt.%)	Ratio of photochrome/fulgide
Na <sup>+</sup>	12	0.21
Ca <sup>2+</sup>	15	0.18
Co <sup>2+</sup>	10	0.23
Ni <sup>2+</sup>	11	0.21
Fe <sup>3+</sup>	13	0.20
Cr <sup>3+</sup>	12	0.17

<sup>4</sup> The tests were carried out in the dark to avoid competitive photocatalysed reactions.



## 3.4. DECOMPOSITION REACTIONS

During preliminary work where the loading of organic on the clay was being investigated using methanol washing, it became apparent that either the *Z* or *E* isomers of the fulgide, or the photochrome, were undergoing some chemical rearrangements to form fluorescent decomposition products. This degradation is extremely important as far as possible applications of clay/fulgide systems are concerned.

Weighed samples of fulgide-treated clays were heated gently in methanol until the washings were colourless. The washings were transferred to a weighed flask, evaporated to dryness and the residue prepared for HPLC analysis by dissolution in a known quantity of hexane/propan-2-ol solvent. Two different procedures were used. In the first, the solid was dissolved in a mixture of 2% propanol in hexane and was eluted through the column with 0.5% propanol in hexane. This gave good separation between the *Z*, *E* and *P* forms, but poor resolution of the decomposition products.

In the second method, the dissolution was carried out in 5% propanol in hexane and elution employed 2.5% propanol in hexane. The peaks for *Z*, *E* and *P* forms overlapped, but well separated peaks for the decomposition products were produced. Calibration of the columns was by use of pure materials.

The rate of degradation of the fulgide or photochrome is very slow. Moreover, in none of our experiments on conversion of the *E* isomer to the photochrome was any trace of such materials found in the external solution.

Our experiments dealt with samples which were 2 years old. They had been stored in the dark, in sealed sample tubes. A typical HPLC trace shows the presence of

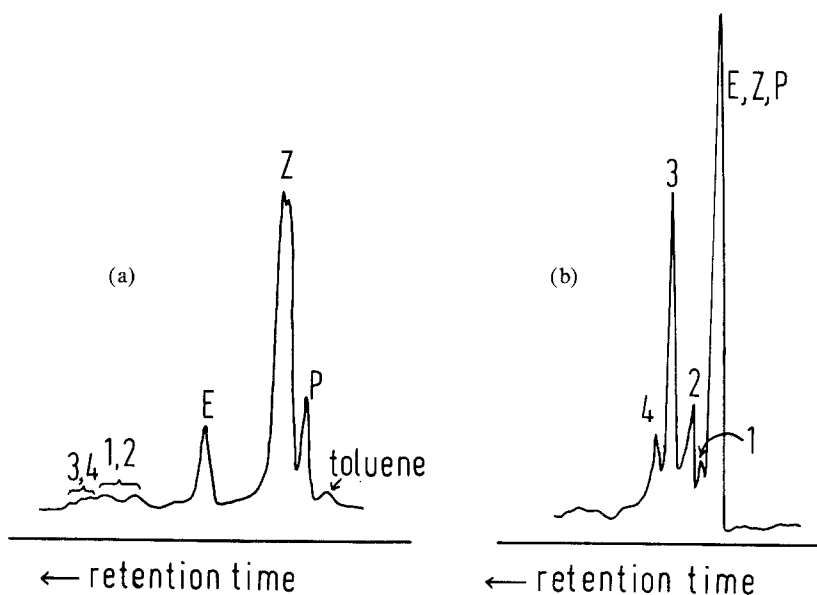


Fig. 10. HPLC traces obtained using the two eluting solvent systems. In (a), there is good resolution of *Z*, *E* and *P* forms of the fulgide, while in (b) the decomposition products are readily separated.

Table VII. Decomposition products

	Clay	Toluene	<i>P</i>	<i>Z</i>	<i>E</i>	DP1	DP2	DP3	DP4
Group B	MON 2	32	5	234	102	1	4	1	1
	3	51	–	24	34	14		8	2
	4	26	68	398	69	18		12	7
	19	22	7	37	20	14		60	9
	20	30	3	81	–	15		29	20
Group A	21	49	48	377	96	–		–	–
	22A	41	16	103	30	–		–	–
	37	23	93	48	30	–		–	–

Table VIII. Decomposition products given by cation exchanged MON 4

Exchangeable cation	<i>Z, E, P</i>	DP1	DP2	DP3	DP4
Na <sup>+</sup>	2332	51	104	250	30
Ca <sup>2+</sup>	4681	78	136	431	24
Ni <sup>2+</sup>	1950		162	384	201
Co <sup>2+</sup>	1843		84	336	74
Cr <sup>3+</sup>	4166	41	269	1111	408
Fe <sup>3+</sup>	3950	33	367	1337	206

four decomposition products (Figure 10). Quantification of the peaks (Table VII) suggested that the decomposition occurs in the clay interlayer region: clays which are known not to intercalate fulgide (Group A) did not give any degradation products.

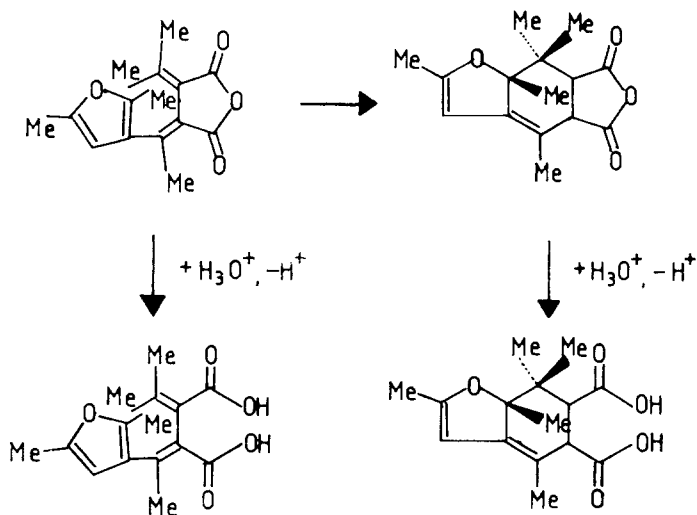
Further tests were carried out on various cation exchanged forms of MON 4. The data indicate (Table VIII) that the concentration of the degradation products increases with the acidity of the clay interlayer region, reaching ~30% of the total organic content in the case of Fe<sup>3+</sup> clays.

### 3.4.1. Product Identification

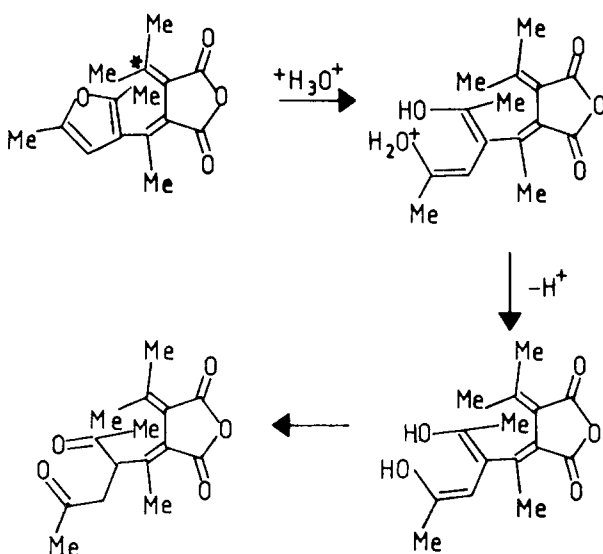
A study of the fulgide molecule reveals two regions where acid attack could take place (Scheme 9). The most obvious of these is hydration of the anhydride ring to yield the diacid, a process which could occur in either of the fulgide isomers or in the photochrome and give, therefore, three distinct products. However, the clay catalysed *Z* → *E* isomerization would mean that the concentration of the *Z* isomer (and hence the corresponding diacid) would be low.

The other region of the molecule which could undergo acid attack is the furan ring. Indeed, ring opening of tetrahydrofuran has been seen to be catalysed by smectites [23]. The resulting dieneol would rearrange to give the diketone (Scheme 10).

The diacids themselves had HPLC retention times much longer than any of the peaks labelled 1–4 on Figure 10. However, it was considered that diacid decomposition products would react with the methanol used to wash material from the



Scheme 9.



Scheme 10.

clay, to give a variety of possible half esters. Some half esters of the *E* and *P* forms were produced by cleavage of the anhydride ring using sodium methoxide and methanol. The retention times were similar to those of peaks 3 and 4. Moreover, it was observed that the photochrome undergoes ring opening to yield fulgide if left to stand (in the light) in the solvent mixture for any length of time. At the same time there was a transfer of intensity from peak 3 to peak 4, again supporting the suggestion that the various diacids are the main decomposition products.



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