

Diels–Alder Reactions Catalysed by Cation-exchanged Clay Minerals

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Catalysis of Diels–Alder reactions by various clay minerals exchanged with a variety of transition metal cations was shown to occur readily at ambient temperatures in a variety of solvents. Non-transition and lanthanide cation-exchanged clays were found to be ineffective. α,β -Unsaturated carbonyl compounds (such as methyl vinyl ketone, methyl acrylate and methyl methacrylate) were used as dienophile. Cyclopentadiene, furan, pyrrole, isoprene and cyclohexa-1,3-diene were successfully employed as the diene, whilst thiophene was unreactive. Such reactions (except that with isoprene which produces a mixture of 1,3- and 1,4-isomers) produced a mixture of *endo*- and *exo*-isomers, the ratios of which could be altered by manipulation of the inter-layer reaction space of the clay catalyst. Choosing a clay with a higher layer charge, and hence lower basal spacing, Δd , gave increased selection for the kinetically less favoured, but less bulky isomer.

With the current emphasis in organic synthesis on control of the regioselectivity and stereoselectivity of reactions we decided to investigate the effects of clay catalysts, which in the past have been shown to be highly product-selective,^{1–3} on the regioselectivity of certain reactions. The first type of reaction chosen was the Diels–Alder reaction due to the wide ranging specificity encountered with these reactions.⁴ The Diels–Alder reaction is a concerted electrocyclic ($4\pi + 2\pi$) reaction that often needs catalysing and is generally the method of choice in the synthesis of 6-membered rings.

Lewis acid complexation of the dienophile can enhance the rate of the reaction,^{5,6} often by as much as a factor of 10^6 , and can even allow reactions to proceed at very low temperatures. The mode of action of the Lewis acid appears to involve coordination of the carbonyl group of the unsaturated ketone to the metal, thus causing the carbonyl group to become more electron-withdrawing. This has the effect of lowering the energy level of the LUMO (Lowest Unoccupied Molecular Orbital) of the dienophile, enabling more efficient overlap with the HOMO (Highest Occupied Molecular Orbital) of the diene. Reaction therefore proceeds with greater ease. Such catalysis serves to increase dramatically the proportion of the kinetically favoured *endo*-isomer, often to as great as 99:1. Polar solvents are most efficient and it has been shown that water as a solvent can increase both the rate and stereoselectivity of the reaction.^{7,8}

A second method of enhancing this Diels–Alder reaction is to include a radical source in the reaction mixture. This forms a highly electron-deficient radical cation from the dienophile and thus enhances both the reaction rate and the proportion of *endo*-isomer in a similar manner to the Lewis acids.

Bauld and Ghosh⁹ used transition metal-exchanged zeolites to catalyse various thermal and photochemical electrocyclic reactions, including the Diels–Alder reaction. These reactions, although very facile and relatively free from side reactions, are limited either to materials which are small enough to be able to enter and leave the zeolite pores, or to materials which can be strongly bound to the outside surface of the zeolite. The layered nature of clay minerals, which allows expansion of the inter-lamellar space if required, places far fewer restrictions on the size and shapes of molecules which may enter the clay and reach the active site for reaction.¹⁰

Laszlo and Luchetti^{11–13} showed that the mixed aqueous/

Table 1 Acid-activated clay catalysed Diels–Alder reactions reported by Laszlo *et al.*^{11–13}

Diene	Clay catalyst	<i>endo:exo</i> Ratio	Time to complete reaction
Cyclopentadiene	Fe ³⁺ -K10	9.0:1	0 °C, 1 h
Cyclopentadiene	K10	9.2:1	
Furan	Fe ³⁺ -K10	2.2:1	6 h
Cyclohexa-1,3-diene	Fe ³⁺ -K10	4.0:1	0 °C, < 1 h ^a
2,5-Dimethylfuran	Fe ³⁺ -K10	0.6:1	5 h

^a Reaction required presence of 4-*tert*-butylphenol.

organic solvent environment created in their acid-activated clay samples (K-10) was highly conducive to promoting Diels–Alder reactions with methyl vinyl ketone. They achieved rate increases of up to 7–8-fold with Fe³⁺-exchanged K-10 (see Table 1), and of 3–4-fold with non-exchanged K-10. Reactions were monitored by gas liquid chromatography and rates were shown to be enhanced by addition of radical sources.^{11–13}

Downing *et al.*¹⁴ have shown that buta-1,3-diene can be cyclodimerised by Cu⁺-exchanged montmorillonite clay. Diels–Alder cyclisations are also involved in the commercially important clay-catalysed dimerisation of oleic acid.¹⁵ There is some doubt as to whether these reactions are truly examples of catalysed Diels–Alder reactions. The former reaction has been shown to occur with non-exchanged Cu⁺ ions¹⁶ and may involve a stepwise metal-coordination mechanism. The latter reaction may simply be a thermal Diels–Alder reaction, unaffected by the clay which serves to catalyse the formation of dienes by isomerisation/dehydrogenation reactions of the oleic acid.

We previously reported some preliminary findings on Diels–Alder reactions catalysed by non-acid-treated cation-exchanged montmorillonite clays,^{10,17} where we found it necessary to exchange the natural calcium or sodium cations in the clay for transition metal cations in order for reaction to proceed.¹⁷ This paper completes that report and details how the catalysis may be extended to other dienes and dienophiles.

Results and Discussion

Due to the convenient isomer distribution and reaction rates involved, the principal Diels–Alder reaction examined was that

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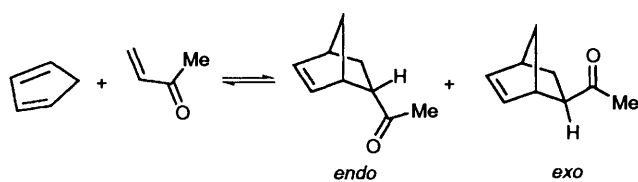


Fig. 1

between cyclopentadiene and methyl vinyl ketone. The reaction produces a mixture of *exo*- and *endo*-isomers as shown (Fig. 1).

The preponderance of the *endo*-isomer in the uncatalysed reaction at room temperature (*ca.* 19:1 *endo:exo*), can be rationalised by observing that a more favourable secondary orbital overlap will occur in the transition state for the *endo*-isomer compared to that for the *exo*-isomer (Fig. 2).⁴ At elevated temperatures, where the effects of secondary orbital overlap become less important, the ratio of isomers approaches unity. Fig. 2 also shows that the transition state for the *exo*-isomer is extended when compared with that of the *endo*-isomer. This makes it flatter and effectively less bulky, which would make its formation more favoured in a restricted environment.

The reaction between methyl vinyl ketone and cyclopentadiene is rather slow at room temperature (see Table 3) and, as mentioned above, several attempts at catalysing the reaction have been successful.

We followed our clay-catalysed reactions by means of ¹H NMR spectroscopy, which afforded a direct measure of both the reaction rate and the ratio of isomers formed. Great care had to be exercised in centrifuging the clay to the bottom of the NMR tube, as the paramagnetic clay resulted in excessive line broadening if it was allowed to remain within the observed region of the NMR spectrometer.

We have previously shown that Diels-Alder dimers can be formed from butadiene and isoprene in the presence of Cr³⁺-exchanged clay.¹⁷ Thus, we investigated the effects of Cr³⁺-exchanged clay on the Diels-Alder reaction of methyl vinyl ketone and cyclopentadiene in dichloromethane as solvent. From Table 3 it is apparent that there is a good rate enhancement with the Cr³⁺-exchanged clay (*ca.* 7–8 fold) and that the *endo:exo* ratio of the products is very similar to that obtained by Laszlo and Luchetti.^{11–13} In view of our results on the importance of the solvent in the catalysis of cyclic anhydride formation by Al³⁺-exchanged clays,³ we investigated whether the reaction rate or isomer ratio was altered by changing the solvent. Table 2 shows the solvents examined together with a measure of the reaction rates, isomer ratios and basal spacing (Δd) values for the clay in that solvent.

With the exception of chloroform, it can be seen from Table 2 that change of solvent has little effect upon the rate of the reaction. This exceptional behaviour is probably due to the fact that the clay clumped together in this solvent and would not remain in suspension. These results are in contrast to the significant solvent effects observed in cyclic anhydride formation.³ Thus it must be concluded that factors other than the solvent are controlling the interlayer spacing whilst this reaction is proceeding.

On examining other cations, only transition metal-exchanged clays produced rate increases (see Table 3). It is noteworthy that although some of the rate increases were modest, *e.g.* with M²⁺-cations, there was often a profound effect upon the *endo:exo* isomer ratio, with this ratio decreasing to *ca.* 5.5:1 with Cu²⁺-exchanged clay.

An interesting result was obtained with both La³⁺- and Al³⁺-exchanged clay. No significant rate increases were seen, but the isomer ratio had decreased to *ca.* 11:1, suggesting that reaction must be occurring in the restricted environment of the interlamellar space. As the acidity of Al³⁺-exchanged clay

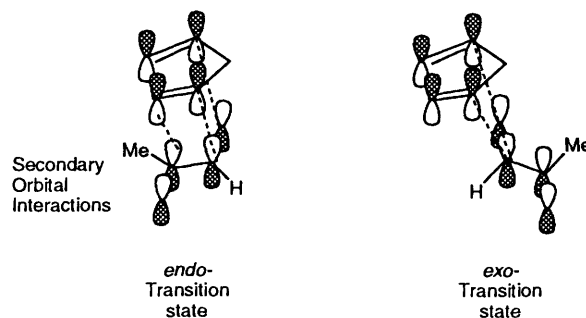


Fig. 2

Table 2 Effects of various solvents on the Cr³⁺-exchanged clay-catalysed Diels-Alder reaction of cyclopentadiene with methyl vinyl ketone

Solvent	% Yield in 20 min	<i>endo:exo</i> Ratio	$\Delta d/\text{\AA}$
Dichloromethane	92	8.5:1	6.8
Chloroform	58	7.0:1	7.5
Benzene	87	9.0:1	8.7
Chlorobenzene	92	9.1:1	7.7
Tetrachloromethane	90	9.2:1	7.5
1,1,2,2-Tetrachloroethane	92	7.0:1	7.8

Table 3 Cation exchanged clay-catalysed Diels-Alder reaction between cyclopentadiene and methyl vinyl ketone

M ⁿ⁺ Clay	% Yield in 20 min	Layer charge ^a	$\Delta d/\text{\AA}$	<i>endo:exo</i> Ratio
No-Clay	17	—	—	19:1
Cr ³⁺ -Tonsil 13 ^b	91	0.37	6.8	9:1
Fe ³⁺ -Tonsil 13	93	0.37	—	7:1
Al ³⁺ -Tonsil 13	20	0.37	—	11:1
Cu ²⁺ -Tonsil 13	28	0.37	—	5.5:1
Co ²⁺ -Tonsil 13	25	0.37	—	6:1
Ni ²⁺ -Tonsil 13	25	0.37	—	5.3:1
La ³⁺ -Tonsil 13	28	0.37	—	11:1
Zr-Pillared Tonsil 13	100 (12 min)	—	6.5	7:1
Fe ³⁺ -K10	97	—	—	9:1
K10	—	—	—	9:1
Cr ³⁺ -RLO1987 ^c	78	0.60	3.2	6:1
Cr ³⁺ -Vermiculite ^d	18	0.65	2.8	2.5:1

^a Charge per (Si, Al)₄O₁₀(OH)₂ unit. ^b A German montmorillonite. ^c A Brett Fuller's Earth. ^d A swelling vermiculite.

is similar to that of Cr³⁺-exchanged clay and greater than that of M²⁺-exchanged clays,^{18,19} these results suggest that the mechanism of the reaction requires a transition metal and does not involve either a Brønsted or a Lewis acid catalysis step (*e.g.* activation of the ketone by protonation or coordination of the carbonyl group).

In contrast with the clean reactions reported by Laszlo and Luchetti^{11–13} with Fe³⁺-exchanged K-10, a similar reaction with Fe³⁺-exchanged clay became very discoloured and ¹H NMR spectroscopy showed a rapid build-up of by-products. However, all other clay-catalysed reactions were relatively free of side reactions, including dicyclopentadiene formation. If methyl vinyl ketone were omitted from the reaction mixture, dicyclopentadiene was formed at a rate much faster than in the absence of clay; thus suggesting that the methyl vinyl ketone is preferentially coordinated to the catalytic site (probably the aquated transition metal ion), excluding the cyclopentadiene and therefore preventing reaction to give the dimer.

Zirconium pillared²⁰ (Table 3) and hydroxy-chromium pillared^{21–23} clays (Table 4) also gave good catalytic rates and

as expected, the *endo:exo* ratio decreased with lower reaction rate. However, the expected correlation with decreasing layer spacing, Δd , was not observed. This suggests that the 'width' of the pillars must be considered as well as their height and that the formation of the less bulky *exo*-transition state becomes more favoured as the size of the interlayer pores becomes more restrictive.

With the failure to control isomer distribution effectively by either change of solvent or pillaring, we investigated other cation-exchanged lamellar minerals with higher layer charges than montmorillonites (see Table 3). Care had to be exercised in the choice of mineral as too high a layer charge could prevent the layers expanding to allow ingress of the reactants. A decrease in *endo:exo* ratio was observed with increasing layer charge of the Cr^{3+} -exchanged mineral. Montmorillonite (layer charge 0.37) gave an *endo:exo* ratio of 9:1, Brett Fuller's Earth (layer charge 0.60) gave 6:1, and the most spectacular decrease was with the Cr^{3+} -vermiculite (layer charge 0.65) which gave a ratio of 2.5:1. This result can be rationalised by the fact that vermiculites differ from montmorillonites and Fuller's Earths in that they are trioctahedral minerals and hence require isomorphous substitution of aluminium for silicon in the tetrahedral layer (which resides next to the interlayer region) to give the layer charge.²⁴ The layer charge in the dioctahedral montmorillonites, however, arises mainly from isomorphous substitution in the central octahedral layer, thus the vermiculite layers will be held together more strongly than with the dioctahedral minerals giving a much more restricted interlayer reaction space.

¹H NMR spectroscopy showed that in these reactions much of the methyl vinyl ketone was adsorbed from solution by the clay and very little is displaced on addition of cyclopentadiene. Thus, it appears the clay preferentially adsorbs the methyl vinyl ketone and that the majority of the reaction occurs at the transition metal site in the interlayer region of the mineral. This was confirmed by the general increase (up to a maximum) in *exo*-selectivity on increasing the relative proportion of clay catalyst (see Table 5).

Other dienes were examined to illustrate the versatility of the catalysis (Table 6 and Fig. 3). Observable rate increases were obtained for furan, pyrrole, isoprene and cyclohexa-1,3-diene, but not (as might be expected) for the more aromatic thiophene.

The reaction with pyrrole gave only 35% Diels-Alder adduct before reaction ceased. This may be due to the secondary amine products being far more coordinating than the aromatic pyrrole and these products may then either ligate to the metal ions or simply become protonated and remain at the active sites. In either case the products would remain in the interlamellar region and prevent further ingress of reactants.

Isoprene and cyclohexa-1,3-diene with methyl vinyl ketone in the presence of Cr^{3+} -exchanged clay were also examined. The reactions were complete in 20 min at room temperature, in contrast to 3 d for the uncatalysed reactions. The isomer ratios for the two sets of products are given in Table 6 and all reactions were complete in 2.5 h, in contrast to about 3 d uncatalysed.

The reactions of three other dienophiles with cyclopentadiene were examined. The highly conjugating, and thus highly electron-withdrawing properties of carbonyl (and other) functional groups, lowers the relative energy of the LUMO of the dienophile, thus allowing more efficient overlap with the diene HOMO.⁴ Such dienophiles react at enhanced rates relative to non-conjugated dienophiles such as allyl chloride, which has little activation through the inductive effect of the chlorine. As might be expected, the poorly activated dienophile, allyl chloride, did not react under the usual conditions (room temperature, dichloromethane solvent) even with one of our more reactive catalysts, Cr^{3+} -exchanged Tonsil 13. Elevated

Table 4 Hydroxy-chromium-pillared Tonsil 13 catalysis of the Diels-Alder reaction between cyclopentadiene and methyl vinyl ketone

Ratio of equivalents of base:Cr	Colour of clay	% Yield in 20 min	<i>endo:exo</i> Ratio	$\Delta d/\text{\AA}$
0.0 (<i>i.e.</i> Cr^{3+} -clay)	Grey/blue	90	9:1	4.08
0.5	Grey/green	55	5.0:1	5.59
1.0	Light khaki green	42	4.5:1	6.18
1.5	Dark green	59	5.5:1	16.69
2.0	Light green	66	6.0:1	13.20

Table 5 Effect of varying the proportion of clay catalyst on the *endo:exo* isomer ratio of the Diels-Alder reaction between cyclopentadiene and methyl vinyl ketone

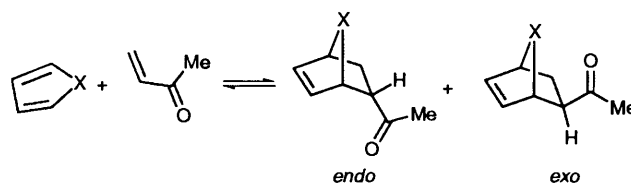
Mass of clay/mg ^a	62.5	125	187.5	250 ^b	500
<i>endo:exo</i> ratio Cr^{3+} -Tonsil 13	11:1	8:1	8:1	9:1	9:1
<i>endo:exo</i> ratio Cu^{2+} -Tonsil 13	8:1	9.5:1	4.5:1	5.5:1	5.5:1

^a 3.1 mmol of each reactant in 5 cm³ dichloromethane at 25 °C. ^b An equivalent amount to that used in the usual NMR experiments.

Table 6 Cr^{3+} -Tonsil 13 catalysis of the Diels-Alder reaction between various dienes and methyl vinyl ketone

Diene	% Yield @ 20 min ^a	<i>endo:exo</i> Isomer ratio	Uncatalysed reaction ^b
Furan	14	3.0:1	no reaction
Pyrrole	35	4.0:1	no reaction
Thiophene	0	—	—
Isoprene	35	3.0:1	no reaction
Cyclohexa-1,3-diene	72	8.1:1	20%

^a 3.1 mmol of each reactant in 5 cm³ dichloromethane at 25 °C. ^b After 2 days at 25 °C.



Where X = $[\text{CH}_2]_2$, NH or O, but not S

Fig. 3

temperatures simply increased the rate of dimerisation of the cyclopentadiene.

Methyl acrylate did not react cleanly with Cr^{3+} -exchanged montmorillonite as catalyst unless the clay was carefully deferrated by the method of Van Leemput and Stuhl,²⁵ before chromium exchange. This problem may be due to the methyl acrylate polymerising on exposed Fe^{3+} -cations at the edge of the clay layers and hence blocking access to the clay interlayer. However, when the clay had been deferrated, the expected Diels-Alder adducts were formed with an *endo:exo* ratio of 3:1; this compares with a ratio of *ca.* 5:1 for the uncatalysed reaction. Even with deferrated clay catalysts, methyl methacrylate gave no Diels-Alder adducts with cyclopentadiene. This is in accord with the reported rapid polymerisation of this dienophile in the presence of clays.²⁶

At first it appeared that the mechanism of the catalysis might involve one electron transfer from the dienophile to the transition metal cation. This was supported by the observation that the intensity of the ESR signal from a Cu^{2+} -exchanged

clay, suspended in dichloromethane, decreased (paramagnetic $\text{Cu}^{2+} + e^- \rightarrow \text{diagnostic Cu}^+$) on addition of methyl vinyl ketone and partially re-established itself on addition of cyclopentadiene. Unfortunately, other transition metal-exchanged clays did not give intense enough ESR signals for similar observations to be made. However, the redox potentials of both Cr^{III} and Zr^{IV} are very much less readily accessible ($\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$ and $\text{Zr}^{4+} \rightarrow \text{Zr}^{3+}$)²⁷ than those of Cu^{II} or Fe^{III} ($\text{Cu}^{2+} \rightarrow \text{Cu}^+$ and $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$)²⁷ and so such a mechanism would be unlikely with the former cations. Both Lewis and Brønsted catalysis were excluded earlier due to the inactivity of Al^{3+} - and La^{3+} -exchanged clays. This leaves the possibility that the d-orbitals on the transition metal may simply be involved in constraining the dienophile and diene into a suitable configuration enabling reaction to occur at an increased rate.

Conclusions.—A wide range of transition metal-exchanged clay minerals are good catalysts for Diels–Alder reactions which involve α,β -unsaturated carbonyl compounds (such as methyl vinyl ketone and methyl acrylate) as dienophile. Problems occurred with methyl acrylate which required deferration of the clay in order for a clean reaction to be obtained. Methyl methacrylate did not give a Diels–Alder adduct, probably due to polymerisation on the edge of the clay particle. A number of simple cyclic and acyclic dienes (cyclopentadiene, cyclohexa-1,3-diene and isoprene) successfully undergo reaction, as have some heterocyclic dienes (furan and pyrrole). The proportion of the kinetically less favoured, but less bulky, *exo* isomer may be improved by choosing a clay mineral which has a higher layer charge, and thus narrower interlamellar space, in which to carry out the Diels–Alder reaction. Increasing the proportion of the clay catalyst can increase the proportion of the less bulky *exo* isomer obtained.

Experimental

Catalyst Characterisation.—The bentonite used for most of this study came from Moosburg, West Germany (Tonsil 13, Süd-Chemie AG). The $< 2 \mu\text{m}$ clay fraction was selected by sedimentation. An XRD examination showed that this fraction was ca. 98% montmorillonite with ca. 2% quartz impurity. An XRF analysis gave 64.0% SiO_2 ; 20.8% Al_2O_3 ; 3.86% Fe_2O_3 ; 0.07% TiO_2 ; 1.5% CaO ; 1.42% MgO ; 0.04% K_2O ; and 1.20% Na_2O . The loss on ignition was 7.1%. The cation exchange capacity (CEC) totalled 103 meq/100 g of air-dry material, made up of 68, 33 and 2 meq/100 g of Na^+ , Ca^{2+} and Mg^{2+} , respectively.

The K10 catalyst is derived from the Tonsil 13 clay by acid treatment. It has nitrogen surface area of ca. $250 \text{ m}^2 \text{ g}^{-1}$.

The Brett Fuller's Earth and the vermiculite were prepared in a similar manner to the Tonsil 13.

Catalyst Preparation.—(a) *Cation exchanged clays.* To aid later cation exchange processes, a large quantity of either the Tonsil 13 or the Brett Fuller's Earth clay were given a preliminary cation exchange with excess Na^+ . The clays were added to a 0.1 mol dm^{-3} solution of NaCl and heated to 70°C with vigorous stirring for 1 h. Upon sedimentation it was immediately apparent that there were two fractions, the finer material of which was subjected to ultrasonic treatment for 10 min, and the $< 2 \mu\text{m}$ fractions were collected by sedimentation.

The cation exchanges were carried out by dissolving the metal chlorides (10 fold molar excess, based on the CEC of the clays) in deionized water (40 cm^3 per g of clay), after which the clays were added, and the temperature raised to 70°C for 1 h. Repetitive centrifugation and resuspension was then carried out until the solutions were free of chloride. The clays were then dried at 80°C for ca. 15 h and ground before use. Fe^{3+} -K10

samples were produced in a manner similar to that above, but without the preliminary Na^+ -exchange.

(b) *Pillared clays.* Zirconium pillared²⁰ and hydroxy-chromium pillared^{21–23} clays were prepared by their respective literature methods.

Pot Reactions.—In large scale experiments the reaction conditions were either:

(a) Clay (0.5 g); solvent (50 cm^3); dienophile (10 cm^3) and diene (equimolar amount), or (b) clay (0.5 g); solvent (10 cm^3) and each reactant (ca. 0.2 g).

In all cases the dienophile was stirred with the clay in the solvent before adding the diene. The clays were filtered off after completion of the reactions, the residue washed with an equal volume of pure solvent and the combined organic solutions evaporated to dryness under reduced pressure. Yields in excess of 90% were generally obtained.

Reactions Carried Out in the NMR Spectrometer.—The rates of the reactions were conveniently studied by NMR spectroscopy. We developed a suitable method for studying the processes *in situ*:

The 5 mm NMR tube was charged with clay (0.025 g) and solvent (0.5 cm^3) and sealed. After 5 min shaking (for homogenisation) the dienophile (20 mm^3) was injected and further shaking was carried out (5 min). Then the diene (20 mm^3) was injected, and the NMR tube shaken manually.

The reaction was followed with time. Before each NMR spectrum was recorded the NMR tube was centrifuged to sediment the clay. Between spectra the tube was shaken vigorously using a mechanical shaker. The rate of formation of products was calculated by using the integrals of the methyl protons on the dienophile and products. In the case of cyclopentadiene dimerisation the rate of loss of the cyclopentadiene CH_2 group signal was monitored.

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