Dimerisation of olefins catalysed by K10-montmorillonite clays

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K10- as well as cation-exchanged montmorillonite clays are found to catalyse efficiently the dimerisation of *trans*-stilbene, 1,1-diphenylethylene and α-methylstyrene, in a reaction involving carbocationic intermediates.

KEY WORDS: montmorillonites; catalysis; olefins; dimerisation

1. Introduction

Clays are aluminosilicates with a layered structure and due to the interlayer microenvironment are effective heterogeneous catalysts for a wide variety of organic reactions [1,2]. Montmorillonite clays [3], which are dioctahedral phyllosilicates, with an octahedral layer (AlO_6 units) sandwiched between two tetrahedral layers (SiO_4 units), are extensively employed in many clay-mediated reactions [4].

Alkenes, when placed in clay interlayer, generally undergo acid-catalysed reactions such as isomerisation, rearrangement, oligomerisation and addition across the double bond with suitable nucleophiles [5]. However, the utility of clays as a medium for dimerisation of olefins is not explored in detail, barring a preliminary report [6]. This has prompted us to carry out a detailed investigation on the dimerisation of *trans*-stilbene and related compounds in clay microenvironment.

While the isomerisation of *trans*-stilbene is extensively studied in acidic conditions, its dimerisation is found to be elusive. Thermal dimerisation of *trans*-stilbene in the presence of concentrated mineral acids and metal halides results in the formation of tetralin and indane derivatives under very rigorous conditions [7]. However, the corresponding photochemical dimerisation yields cyclobutane derivatives [8]. In an earlier work [6] on dimerisation of *trans*-stilbene catalysed by copper(II)-ion-exchanged montmorillonite clay the formation of a material (m/e 360) corresponding to the dimer is reported. Based on the mass spectral evidence it is postulated as tetraphenylcyclobutane. In the present study, results of our experiments on utility of acidic montmorillonites, as efficient solid acid catalysts for dimerisation of *trans*-stilbene, 1,1-diphenylethylene and α-methylstyrene, are presented.

2. Experimental

2.1. Reagents and catalysts

Trans-stilbene (Aldrich, AR), α-methylstyrene (Aldrich, AR) and 1,1-diphenylethylene (E. Merck, AR) were used as such. K10-montmorillonite clay obtained from Aldrich was used as received and cation-exchanged clays were prepared as reported earlier [9]. GC analysis of the reaction mixture was carried out in a Shimadzu 17A GC instrument (SE-30 5% column, FID detector and high purity nitrogen as the carrier gas). ^{1}H-NMR spectra of the separated fractions were recorded in a 200 MHz Bruker instrument. GC-MS of the reaction mixture was recorded in a Shimadzu QP-5050A instrument with DB-5 column and high purity helium as the carrier gas.

2.2. Dimerisation of trans-stilbene (I)

50 mg of *trans*-stilbene was mixed intimately with 200 mg of Fe^{3+}-exchanged K10-montmorillonite clay. The reaction mixture was heated in an oil bath at 160 °C for 10 min. It was cooled and extracted with dichloromethane and evaporated on a water bath. The residue was analysed by TLC and also by GC. The products were separated by column chromatography using a petroleum ether–ethyl acetate (9 : 1) mixture as eluant and were characterised by comparison with their ^{1}H-NMR spectra reported earlier [7].

2.3. Dimerisation of α-methylstyrene (V) and 1,1-diphenylethylene (VII)

50 mg of α-methylstyrene (V) and 200 mg of Fe^{3+}-exchanged K10-montmorillonite clay were heated in an oil bath at 115 °C for 15 min. The reaction mixture after extraction with acetone was analysed by TLC. The dimer was isolated by column chromatography using petroleum ether as the eluant and the crude dimer (VI) was recrystallised from

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Table 1
Percentage conversion and products distribution[a] in clay-catalysed dimerisation of *trans*-stilbene.

Clay	Time (min)	Conversion (%)	Percentage of products II[b]	III	IV	X[c]
Fe^{3+}-Mont.	10	100	8	42	40	10
Al^{3+}-Mont.	15	100	8	42	38	12
H^{+}-Mont.	60	100	7	40	40	13
Cu^{2+}-Mont.	90	100	–	48	43	9
Mg^{2+}-Mont.	180	80	5	32	37	6
Ca^{2+}-Mont.	180	70	4	28	30	8
Na^{+}-Mont.	180	40	3	16	15	6

[a] Analysed by preparative TLC/GC; error limit ±5%.
[b] For structures of II–IV, see scheme 1.
[c] Unidentified products.

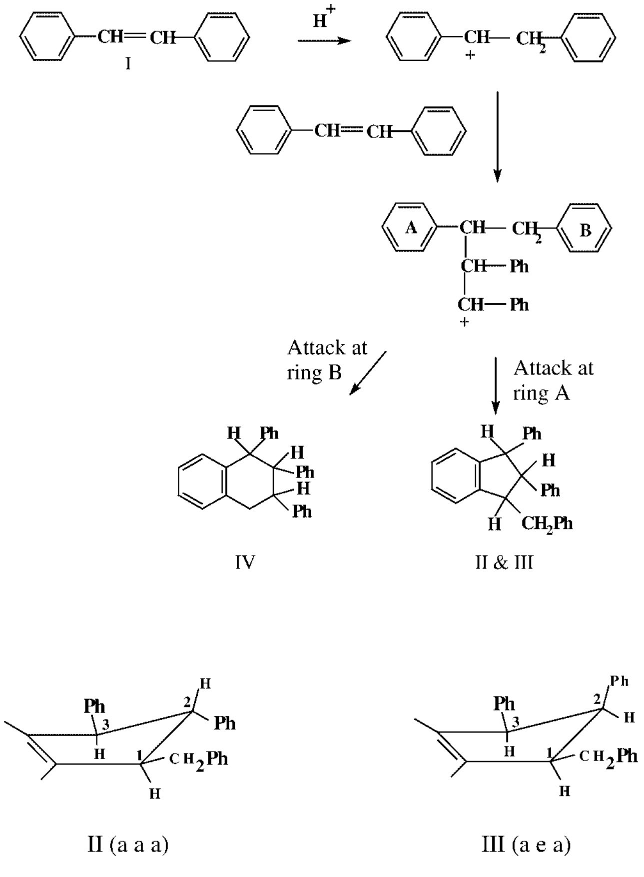
acetone–methanol mixture. It was characterised by its ^{1}H-NMR spectra. The NMR data for (VI): δ 1.57 (s, 6H), δ 1.69 (s, 3H), δ 2.17 (s, 2H) and δ 7.0 (m, 9H).

The dimerisation of 1,1-diphenylethylene (VII) was carried out at 90 °C by a similar procedure as described for (V). The crude dimeric product (VIII) was recrystallised from acetic acid and was characterised by its ^{1}H-NMR spectrum (δ 1.5 (s, 3H), 3.2 (quartet, AB pattern, 2H) and 7.0 (m, 19H)).

3. Results and discussion

3.1. Dimerisation of trans-stilbene

Trans-stilbene undergoes efficient dimerisation in the presence of acidic clays such as Fe^{3+}-exchanged K10-montmorillonite. 100% conversion of the starting material is observed and a mixture of three cyclic dimers is identified (table 1). They are separated by column chromatography and ^{1}H-NMR spectra of these compounds are recorded. Of the three fractions II is found to be an indane derivative by comparison with its ^{1}H-NMR data reported earlier [7]. Compound III is also identified as an isomer (a e a) of II (a a a) by comparison with its ^{1}H-NMR spectrum [7]. The spectrum of fraction IV largely resembles that of the tetralin derivatives [7]. Indane derivatives II and III are also identified by a characteristic (M-91) peak at 269 mass units in the GC-MS spectrum, while this peak is absent in IV. The reaction mixture also contains about 10% of unidentified products (which show MI peaks at 340 and 344 mass unit). It is relevant to note that the (M-91) peak at 269 mass units is also observed in significant intensity in the copper(II)-exchanged montmorillonite-catalysed dimerisation of *trans*-stilbene reported earlier [6], and this can be construed as additional evidence for the formation of only indane and tetralin derivatives. It is significant to observe that no cyclobutane dimers are formed in this clay-catalysed dimerisation, as literature reports [8], of the cyclobutane dimers show that they have melting points of 163 and 150 °C and their ^{1}H-NMR data are also significantly different.



Scheme 1. Clay-catalysed dimerisation of *trans*-stilbene (I).

Dimerisation with other cation-exchanged montmorillonites are also carried out at the same temperature and similar results are obtained. While H^{+}- and M^{3+}-exchanged montmorillonite clays are found to be very efficient, the reaction takes a longer time to complete in the case of M^{2+}-exchanged montmorillonite clays (table 1). The reaction is the slowest of the lot with the Na^{+}-exchanged montmorilonite clay. These results indicate an active role for the Brønsted acidity within the clay interlayer in the dimerisation reaction and the following mechanism involving carbocationic intermediates is proposed (scheme 1). Protonation of *trans*-stilbene gives a stilbonium cation, which then combines with another neutral molecule of *trans*-stilbene giving rise to the dimer cation. Subsequent cyclisation of the dimer cation leads to either an indane or a tetralin derivative, as shown in the scheme 1.

3.2. Dimerisation of α-methylstyrene

Dimerisation of α-methylstyrene is carried out in the presence of Fe^{3+}-exchanged K10-montmorillonite clay. The reaction is complete in 10 min. When the acetone extract is concentrated, the dimer has separated out as a white solid upon addition of methanol. It is filtered and recrystallised from acetone–methanol mixture (melting point 111 °C). From its ^{1}H-NMR spectrum it is identified as the indane derivative. The dimerisation is also carried out in the presence of other cation-exchanged montmorillonite clays

Table 2
Percentage conversion[a] and product distribution in the clay-catalysed dimerisation of α-methylstyrene (V) and 1,1-diphenylethylene (VII).

Clay	α-methylstyrene			1,1-diphenylethylene		
	Time (min)	Conversion (%)	Yield of VI[b]	Time (min)	Conversion (%)	Yield of VIII[b]
Fe^{3+}-Mont.	10	100	75	15	100	70
Al^{3+}-Mont.	15	100	68	20	100	72
H^{+}-Mont.	10	100	69	15	100	68
Cu^{2+}-Mont.	90	100	74	120	80	65
Mg^{2+}-Mont.	180	100	72	180	80	66
Ca^{2+}-Mont.	180	100	69	180	80	68
Na^{+}-Mont.	180	80	70	180	70	62

[a] Analysed by preparative TLC/GC; error limit ±5%.
[b] For structures of V–VIII, see scheme 2. Isolated yield of VI/VIII.

(table 2) and the same single product is observed (75% isolated yield) in all the cases.

3.3. Dimerisation of 1,1-diphenylethylene

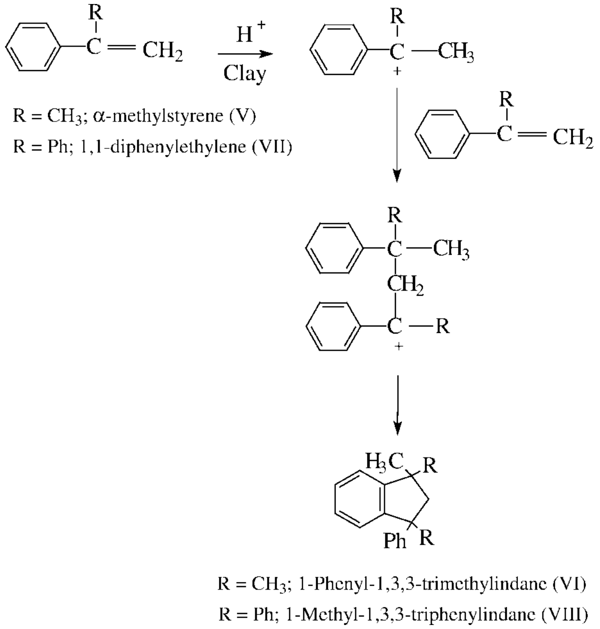
1,1-diphenylethylene also dimerises efficiently in the presence of Fe^{3+}-exchanged K10-montmorillonite clay at 90 °C and 100% conversion is observed in 15 min. The development of a bluish green colour, upon addition of the olefin, is indicative of the formation of the dimer cation [10]. Here also only one product is formed predominantly (70% isolated yield). The colourless solid is washed with acetone and recrystallised from acetic acid (m.p. 140 °C). From the ^{1}H-NMR spectrum of the sample, it is identified as an indane derivative [11]. The dimerisation is carried out with other cation-exchanged K10-montmorillonite clays also (table 2) and the same product is obtained in each case. The prominent formation of indane derivatives in both α-methylstyrene and 1,1-diphenylethylene is rationalised on the basis of a suitable mechanism (scheme 2) involving attack of the dimer cation on the *ortho* position of the first aryl ring leading to cyclisation. This is in contrast to 1,2-diphenylethylene, namely stilbene, wherein an alternative attack at the farther aryl ring is also likely and can lead to a tetralin derivative.

4. Conclusions

(a) Dimerisation of 1,2-diphenylethylene (stilbene), 1,1-diphenylethylene and α-methylstyrene proceeds efficiently in the presence of acidic clays catalysed by their Brønsted acidity. Isomeric indane and tetralin derivatives (involving attack of the dimer cation on the nearer and farther aryl rings) are formed in equal amounts. However, with 1,1-disubstituted ethylenes (V and VII), the absence of alternative attack by the dimer cation results in the exclusive formation of the indane derivatives.

(b) Cyclobutane derivatives are not obtained and the reaction is obviously controlled by the stability of the carbocations.

(c) Both H^{+} as well as M^{3+}-exchanged clays are found to be very efficient and the reaction takes a longer time with M^{2+}-exchanged clays. A comparison with the earlier work [7] shows that the dimerisation of these olefins proceed at a much faster rate in clay microenvironment. Stringent conditions such as high vacuum, very high temperature, etc., are not needed. Other advantages include simpler work-up, selectivity, milder conditions and eco-friendliness, etc.



Scheme 2. Dimerisation of α-methylstyrene (V) and 1,1-diphenylethylene (VII) catalysed by clays.

Attempts to prepare crossed dimers from two different olefins (e.g., from α-methylstyrene and 1,1-diphenylethylene) have not yielded the desired results. Addition of 1,1-diphenylethylene onto K10-montmorillonite imparts a green colour to the clay sample. Further addition of styrene followed by extraction shows only peaks due to dimers from the individual olefins and no crossed-dimer is formed. Addition of styrene followed by 1,1-diphenylethylene has also yielded the similar result, indicating that both the olefins show preference to their own monomer. It is also likely that diffusion inside the solid sample is difficult under the experimental conditions.

The dimerisation studies when extended to styrene, yield only oligomeric products predominantly under the experimental conditions.

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