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CLAY-CATALYSED ASYMMETRIC DIELS-ALDER REACTION OF CYCLOPENTADIENE WITH (-)-MENTHYL ACRYLATE

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Abstract: Zn(II)-exchanged K10 montmorillonite is shown to be an efficient catalyst for the reaction between cyclopentadiene and (-)-menthyl acrylate, leading to the 1R,2R-cycloadduct with good chemical yield, high % d.e. and excellent endo/exo selectivity.

The Diels-Alder adducts of acrylic acid derivatives constitute an important class of compounds as key intermediates for the total synthesis of a variety of natural products[1].

Excellent diastereofacial selectivities have been achieved in asymmetric Diels-Alder reactions between prochiral 1,3-dienes and chiral acrylates[2]. However, these good results are only obtained when a Lewis acid is used as a catalyst, the Lewis acid being necessary to control the s-cis/s-trans equilibrium of the enoate moiety of the dienophile. The Diels-Alder reaction of (-)-menthyl acrylate with cyclopentadiene has been extensively studied due to the availability of the chiral auxiliary[3] and can be taken as a model reaction for the study of new catalytic systems.

It has been shown that the Diels-Alder reaction can be catalysed by inorganic solids, such as silica gel[4], magnesium silicate[5], alumina[5,6] and clays[7].In particular Laszlo and coworkers[7] have shown that Fe^{3+}-doped K10 montmorillonite is useful for reaction of carbonyl-containing dienophiles.

In this communication we want to describe our preliminary results in the first clay-catalysed asymmetric Diels-Alder reaction. Cation exchanged montmorillonites were prepared by gradually adding the K10 montmorillonite to stirred ferric or zinc chloride solutions (125 ml, 1M) at room temperature following the procedure reported by Laszlo et al[6d]. The suspensions were stirred for 24 h, filtered and washed with deionised water until chemical tests showed that the washings were free of the chloride anion. The resulting cation-exchanged montmorillonites were dried overnight in a thin bed at 120°C in an oven and ground in a mortar. The catalysts were equilibrated over saturated salt solutions in order to give reproducible contents of water.

(-)-Menthyl acrylate was made to react with cyclopentadiene in the presence of a preweighed amount of cation-exchanged montmorillonite dried at 120°C in an oven overnight prior to use (Figure 1).

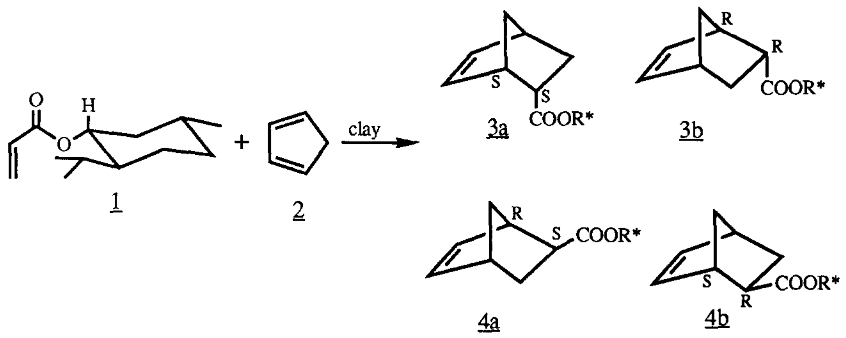

Figure 1

The reaction was monitored by gas chromatography (Hewlett-Packard 5890 II with a flame ionisation detector, cross linked methyl silicone column 25m x 0.2mm x 0.3μm, helium as a carrier gas 18 psi, injector temperature 230°C, detector temperature 250°C, oven temperature programme 190°C (1 min), 2°C/min, 180°C (0 min), 1°C/min, 170°C (5 min), retention times: (1) 3.8 min, (4a)+(4b) 18.4 min, (3a) 19.1 min, (3b) 19.6 min.) The flame ionisation detector was calibrated by repetitive injection of mixtures of (-)-menthyl acrylate and cycloadducts, at different relative concentrations. (3a) and (3b) were assigned by comparison of the gas chromatograms obtained in the clay-catalysed reactions with those obtained in several reactions of cyclopentadiene and (-)-menthyl acrylate using Lewis acids as catalysts, whose results of diastereoselectivities and absolute configurations are described in papers previously published by Oppolzer and coworkers[3c].

Exchanged cation	2 : 1	clay : 2 (g/mmol)	Solvent	T (°C)	t (h)[a]	yield(%)[b]	3 : 4[b]	3b : 3a[b,c]
-	3	-	CH_2Cl_2	20	51	60	79:21	53:47
Zn(II)	3	0.5	CH_2Cl_2	20	24	40	88:12	63:37
Zn(II)	6	0.5	CH_2Cl_2	20	48	70	88:12	62:38
Zn(II)	3[d]	0.5	CH_2Cl_2	20	48	63	92:8	62:38
Zn(II)	6[d]	1.0	CH_2Cl_2	-25	54	66	96:4	75:25
Zn(II)	7.5[e]	1.5	CH_2Cl_2	-25	33	75	95:5	72:28
Zn(II)	12[f]	1.5	CH_2Cl_2	-58	96	33	97:3	79:21
Zn(II)	7.5[e]	1.5	Toluene	-20	48	88	96:4	76:24
Fe(III)	7.5[e]	1.5	CH_2Cl_2	-20	27	20	95:5	76:24

[a]. From this time on further progress of the reaction was not observed. [b]. Determined by gas chromatography. [c]. 3b is preferably obtained. [d]. Diene is added in amounts of 1 eq. at regular times. [e]. Diene is added in amounts of 1.5 eq. at regular times. [f]. Diene is added in amounts of 3 eq. at regular times.

As can be seen the endo/exo and the diastereofacial selectivities are greatly improved in the presence of clay, but the overall yield obtained with a small amount of clay and 3 eq. of diene is not very high. This is due to a competitive oligomerization of the cyclopentadiene, which eliminates one of the reagents and deactivates the clay. This problem can be solved by using larger amounts of clay and adding the diene in small portions.

As expected a decrease in temperature increases the selectivities obtained but the overall yield diminished.

The solvent plays a capital role in clay-catalysed Diels-Alder reactions, toluene being more efficient than CH_2Cl_2[8]. In the reaction of (-)-menthyl acrylate with cyclopentadiene a high overall yield is obtained, without a decrease in endo/exo and diastereofacial selectivities, when toluene is used as the reaction medium.

The exchanged cation determines the relationship between Lewis and Brønsted acidity in the clay, Zn(II) gives a higher Lewis acidity and a lower Brønsted acidity than Fe(III). In the clay-catalysed reaction of (1) and (2) Fe(III) and Zn(II) give about the same selectivity but the chemical yield is better when Zn(II)-exchanged K10 montmorillonite is used as a catalyst. This may be due to a more favoured oligomerization of cyclopentadiene in the Fe(III)-clay catalysed reactions.

The direction of the asymmetric induction can be explained by the model used in Lewis acid-catalysed reactions of cyclopentadiene and (-)-menthyl acrylate[2]. In this model the dienophile displays an anti enoate conformation where the isopropyl group in the (-)-menthol shields the Re face of the dienophile and the attack of the diene preferentially takes place on the Si face (Figure 2).

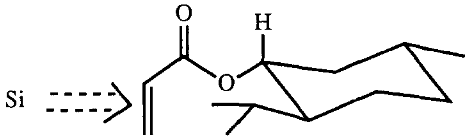

Figure 2

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