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ACCELERATION OF THE DIELS-ALDER REACTION BY CLAYS SUSPENDED IN ORGANIC SOLVENTS

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Abstract : Rapid and stereoselective Diels-Alder reactions can be run in ethanol or methylene chloride in the presence of Fe^{III}-doped K10 montmorillonite.

IMPRESSIVE improvements of the Diels-Alder reaction have been achieved recently. Bauld *et al.*[1] have obtained dramatic accelerations of otherwise sluggish reactions between unactivated hydrocarbon reactants using an $Ar_3N^{+\cdot},SbCl_6^-$ catalyst. We have emulated these results with a less expensive catalyst, consisting of Fe^{III}-doped K10 montmorillonite combined with 4-*t*-butylphenol (10%)[2]. Lewis acids are known to activate oxygen-containing dienophiles[3]. Another breakthrough has been pioneered by Breslow *et al.*[4] and further explored and exploited by the Grieco group[5] : use of water as a solvent leads to greatly enhanced reaction rates and selectivities. The recent appearance of another communication from the Columbia group on this topic[6] prompts us to disclose our results. These are part of a more general program for devising new synthetic procedures that are selective, efficient, mild, easy to run, and inexpensive[7-10]. Our rationale here is to try and take advantage of the joint presence in a clay of pools of water internal to the layered structure (approximately 400 mg per reaction run under the conditions of Table 1), and of Lewis acidic sites for the catalysis of Diels-Alder cycloadditions involving an oxygen-containing dienophile.

We use for this purpose the acidic montmorillonite K10 doped with Fe^{III} [11]. We were pleased indeed to obtain in organic solvents faster reactions with comparable stereoselectivities to those reported in water solution[6] for the cycloaddition between cyclopentadiene and methylvinylketone (MVK). Because temperature is known to affect the exo/endo ratios[3c], we have tested also the importance of this factor (Table 1).

conditions[a]	isolated yield (%)	endo/exo
H_2O, 20°C, 0.3 h	95	19:1 [b]
H_2O, 0°C, 2 h	91	19:1
CH_2Cl_2, 20°C, 0.3 h	97	9:1
CH_2Cl_2, 0°C, 2 h	98	13.5:1
CH_2Cl_2, -24°C, 4 h	96	21:1
C_2H_5OH, 20°C, 0.3 h	95	14:1
C_2H_5OH, 0°C, 1 h	75	25:1
C_2H_5OH, -24°C, 4 h	75	24:1

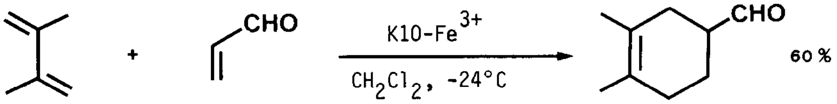
[a] in all cases, 15 mmoles of cyclopentadiene, 15 mmoles of MVK, 2.5 g of K10-Fe^{III} and 50 ml of solvent are used.

[b] the reaction performed in water alone for 3.0 hours leads to a 80% yield of cycloadduct with an endo/exo ratio of 21.4:1[6]

Table 1. Influence of Solvent and Temperature on the Observed Stereoselectivities.

The important finding is of "water-like" accelerations and large stereoselectivities in organic solvents such as, not only protic ethanol, but also methylene chloride, provided the Fe^{III}-doped K10 clay is present (we did the control experiments : in the absence of the clay, the cycloaddition proceeds at much slower rates).

As an illustration, we give below the results for the cycloaddition between 2,3-dimethylbutadiene-1,3 and acrolein :



To sum up, rapid and stereoselective Diels-Alder reactions need not be run in water solution. They can be performed at least equally efficiently in organic solvents in the presence of a clay.

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