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CATALYSIS OF THE DIELS-ALDER REACTION IN THE PRESENCE OF CLAYS

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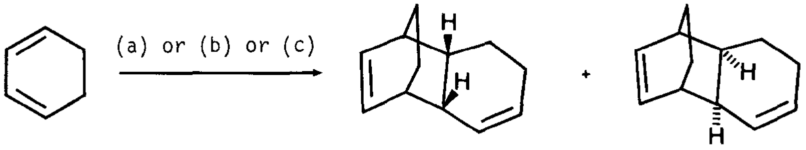
Abstract : Fe^{III}-doped K10 montmorillonite combined with 4-t-butylphenol (10 mol %) is a potent catalytic system for unactivated dienophiles.

The search for the best reaction conditions to make the Diels-Alder reaction fast and stereoselective has recently led to major improvements, on a par with the practical synthetic importance of this choice method for ring formation. Lewis acids can activate dienophiles having an oxygen function[1]. Breslow et al.[2], followed by Grieco et al.[3] have pioneered use of water as solvent : the attendant accelerations and increased stereoselectivities are often considerable. Bauld et al.[4] have shown dramatic accelerations of otherwise sluggish reactions between unactivated hydrocarbon reactants using an $Ar_3N^{+\cdot}SbCl_6^-$ catalyst.

In the context of our on-going design of organic reactions using clays[5-7], we present here our first results on Diels-Alder reactions much improved by the presence of a clay. Our rationale, by analogy with the use of the extremely stable tris (p-bromophenyl) aminium radical cation[4], exploits the propensity of aromatics (phenols especially) to generate radical cations[8] when adsorbed[9] on clay surfaces. We have been able thus to develop an efficient and inexpensive catalytic system for the Diels-Alder reaction, when the dienophile lacks reactivity.

For instance, 1,3-cyclohexadiene 1 placed in the joint presence of an acidic montmorillonite (K10), doped with Fe^{III} [10], and of 4-t-butylphenol (10 mole %) in dichloromethane at 0°C gives cycloadduct 2 with 77% isolated yield in less than 1 h. The presence of the phenol is important (compare entries 2 and 3 in Scheme 1).



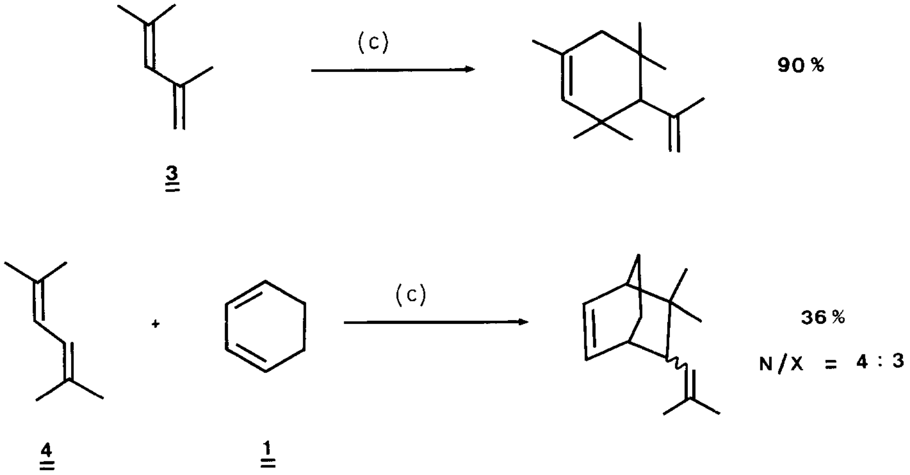
1 2

conditions	isolated yield (%)	endo/exo
(a) 200°C, 20 h	30[11]	4 : 1
(b) K10-Fe^{III},CH_2Cl_2, 0°C, 1 h	49	4 : 1
(c) K10-Fe^{III}, 4-t-butylphenol 10%, 0°C, 1 h	77	4 : 1

SCHEME 1

Of the various montmorillonites we have tested : several natural clays, K10, K10-Zn^{II}, K10-Co^{II}, K10-Al^{III}, K10-Fe^{III}, the latter has proven to be superior.

We have applied successfully reaction conditions (c) to other cycloadditions, such as with 2,4-dimethyl-1,3-pentadiene 3, and with 2,5-dimethyl-2,4-hexadiene 4 added to 1 (Scheme 2).



SCHEME 2

Encouraged by these extremely promising results, we are now exploring the full scope and possible limitations of the Diels-Alder reaction in the presence of clays.

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