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Catalysis of Homo Diels-Alder Reactions By $Yb(fod)_3$

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Summary: The use of $Yb(fod)_3$ to catalyze Diels-Alder reactions of acrolein with sensitive dienes in nearly stoichiometric ratio and with high stereoselectivity is described.

The ability of certain lanthanide complexes to catalyze a variety of hetero Diels-Alder reactions has been described.[1] The mild experimental conditions associated with lanthanide catalysis are helpful in promoting the survival of valuable functionality in the dienophile, the diene and the cycloadduct.[2] Thus, it was of interest to extend this methodology to homo Diels-Alder reactions[3] where acid labile components are to be combined. In this connection, we have examined the Diels-Alder reaction between acrolein and a variety of sensitive dienophiles. Our studies focused on cases where both thermal processes and conventional Lewis acid catalysis have been reported to fail[4] or to exhibit poor stereoselectivity.[5]

Acrolein reacts with acyclic butadienes,[6] under $Yb(fod)_3$[7] catalysis (1.2-1.5 equivalents of diene to acrolein are combined neat at room temperature with $\sim$10 mol % $Yb(fod)_3$ for 24-48 hours) to give the respective cycloadducts in the indicated yields. In the 1-methoxybutadiene case, the only compound isolated was the one derived from endo addition. Cyclopentadiene and furan also react with acrolein under $Yb(fod)_3$ catalysis in a highly stereoselective manner. For example, the cycloadduct formed from acrolein and cyclopentadiene is obtained in 86% yield with an endo:exo ratio 15:1.[5] Even furan undergoes cycloaddition with acrolein at room temperature using $Yb(fod)_3$ as a catalyst. Interestingly, the exo isomer predominates over the endo product in a 4.5:1 ratio.[8]

Other sensitive dienophiles can participate in the $Yb(fod)_3$ catalyzed reaction. This is exemplified by the reaction of crotonaldehyde with cyclopentadiene to give an adduct in an endo:exo ratio of 10:1.[9] For the moment, no Diels-Alder reactions of α,β-unsaturated ketones have been observed.

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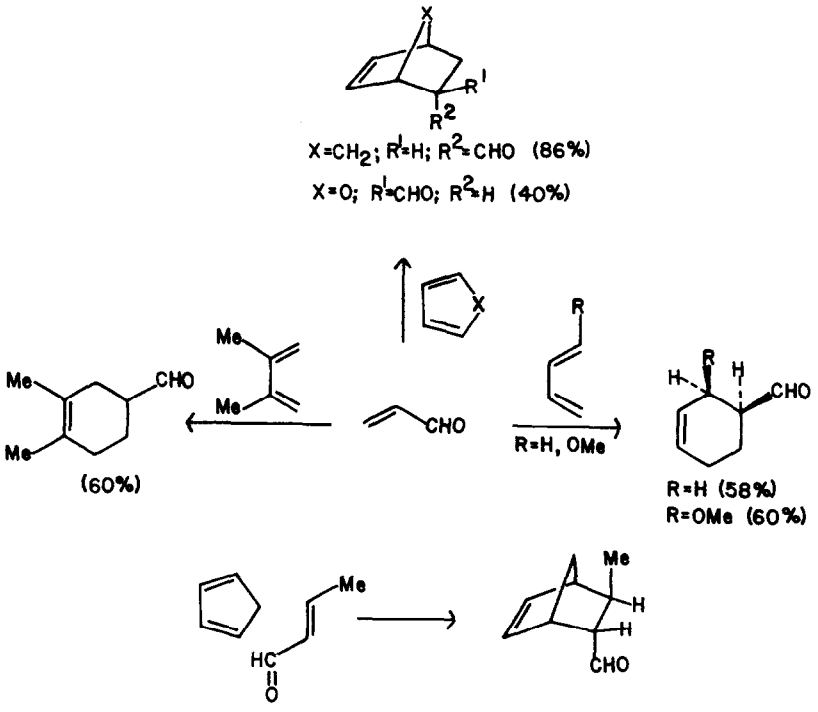

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7. Yb(fod)$_3$ is an abbreviation for [tris(6,6,7,7,8,8,8-hptafluoro-2,2-dimethyl-3,5-ocetanedionate)-ytterbium] and is commercially available from Aldrich.
8. P. Laszlo, J. Lucchetti. Tetrahedron Lett. 25, 4387 (1984) and references cited therein. Our stereochemical results were confirmed by converting the carboxaldehyde function to the exo-2-carbomethoxy-7-oxabicyclo[2.2.1]hept-5-ene and comparing the NMR data of our compound with that in the literature: H. Kotsuki, H. Nishizawa, M. Ochi, K. Matsuoka. Bull. Chem. Soc. Jpn. 55, 496 (1982).
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