

Understanding the influence of Lewis acids in the regioselectivity of the Diels-Alder reactions of 2-methoxy-5-methyl-1,4-benzoquinone: A DFT study

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The mechanisms of the Diels-Alder (DA) reactions of 2-methoxy-5-methyl-1,4-benzoquinone 1 with 2-methyl-1,3-butadiene 2, in the absence and in the presence of LA catalysts, have been studied using the DFT method at the B3LYP/6-31G(d) level of theory. The uncatalyzed DA reactions between 1 and 2 take place via synchronous concerted TSs. The large activation barrier as well as the low stereo and regioselectivity associated with the uncatalyzed process are in clear agreement with the non-polar character of the cycloaddition. Coordination of the LA catalysts, BF₃ or SnCl₄, to the oxygen atoms of the benzoquinone 1 produces a large acceleration of the reaction, which can be associated with the large polar character of the cycloaddition. The different coordination modes of BF₃ and SnCl₄ LA catalysts to the oxygen atoms of benzoquinone 1 allow explaining the reverse para/meta regioselectivity observed in these LA-catalyzed DA reactions. The analysis based on the global and local electrophilic