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# Allylation of Active Methylene Compounds with Cyclic Baylis-Hillman Alcohols: Why Is It Direct and Not Conjugate?

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**Abstract :** Among the carbon-carbon bond formation types, allylation of active methylene compounds with cyclic Baylis-Hillman (BH) alcohols is a reliable and widely used method. This reaction is a very attractive tool in organic synthesis of biological and biodiesel compounds. Thus, in view of an insistent and peremptory request for an efficient and straightly method for synthesizing the desired product, a thorough analysis of various aspects of the reaction processes is an important task. The product afforded by the reaction of active methylene with BH alcohols depends largely on the experimental conditions, notably on the catalyst properties. All experiments reported that catalysis is needed for this reaction type because of the poor ability of alcohol hydroxyl group to be as a suitable leaving group. Within the catalysts, several transition- metal based have been used such as palladium in the presence of acid or base and have been considered as reliable methods. Furthemore, acid catalysts such as BF3.OEt2, BiX3 (X= Cl, Br, I, (OTf)3), InCl3, Yb(OTf)3, FeCl3, p-TsOH and H-montmorillonite have been employed to activate the C-C bond formation through the alkylation of active methylene compounds. Interestingly a report of a smoothly process for the ability of 4-imethyaminopyridine(DMAP) to catalyze the allylation reaction of active methylene compounds with cyclic Baylis-Hillman (BH) alcohol appeared recently. However, the reaction mechanism remains ambiguous, since the C-allylation process leads to an unexpected product (noted P1), corresponding to a direct allylation instead of conjugate allylation, which involves the most electrophilic center according to the electron withdrawing group CO effect. The main objective of the present theoretical study is to better understand the role of the DMAP catalytic activity as well as the process leading to the end- product (P1) for the catalytic reaction of a cyclic BH alcohol with active methylene compounds. For that purpose, we have carried out computations of a set of active methylene compounds varying by R1 and R2 toward the same alcohol, and we have attempted to rationalize the mechanisms thanks to the acid–base approach, and conceptual DFT tools such as chemical potential, hardness, Fukui functions, electrophilicity index and dual descriptor, as these approaches have shown a good prediction of reactions products.The present work is then organized as follows: In a first part some computational details will be given, introducing the reactivity indexes used in the present work, then Section 3 is dedicated to the discussion of the prediction of the selectivity and regioselectivity. The paper ends with some concluding remarks. In this work, we have shown, through DFT method at the B3LYP/6-311++G(d,p) level of theory that: The allylation of active methylene compounds with cyclic BH alcohol is governed by orbital control character. Hence the end- product denoted P1 is generated by direct allylation.

**Keywords :** DFT calculation, gas phase pKa, theoretical mechanism, orbital control, charge control, Fukui function, transition state

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