

Predicting the reaction mechanism of nucleophilic substitutions at carbonyl and thiocarbonyl centres of esters and thioesters

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In nucleophilic substitution reactions at carbonyl centres, there are two possible channels. The first one occurs when the attack of nucleophilic agents takes place simultaneously with the departure of the nucleofuge. This process is named as concerted. The second possibility is the formation of a reaction intermediate, typically a tetrahedral intermediate from which the nucleofuge departs after passing through a second transition state. This second mechanism is defined as stepwise. Whether a concerted or stepwise mechanism is to be expected for a given reaction depends on several factors. Among these determinants are the nucleophilicity of the attacking group, the leaving group ability of the nucleofuge, and the solvent, which affects both the stability of the intermediate or the transition states involved. The role of the electrophilic centre can however become an important factor that can determine the reaction mechanism. In this work we show that the group nucleophilic

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