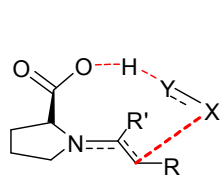


# Mechanistic Studies on Proline Catalyzed Reactions: Enamine Carboxylic Acid vs Enamine Carboxylate/Oxazolidinone Transition State Models

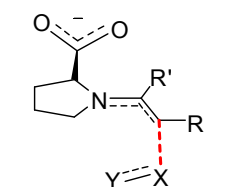
Akhilesh K. Sharma and Raghavan B. Sunoj

Department of Chemistry, Indian Institute of Technology Bombay

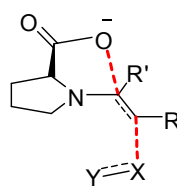
Proline is the one of the earliest known organocatalyst for asymmetric reactions and has seen an unprecedented growth in the last decade. The concept of bifunctional catalysis has been used to develop a variety of proline derivatives. Due to its widespread use in asymmetric synthesis, its mechanism is of utmost importance, and has been explained by combined efforts of experimental and computational studies.<sup>1</sup> The most accepted transition state model for the stereodetermining step is the Houk-List model (a). However, this model was questioned by lack of evidence for enamine formation in the reaction. The detection of oxazolidinone in the reaction mixture led Seebach, Eschenmoser and co-workers propose a transition state model in which oxazolidinone (c) plays an active role.<sup>2</sup> Due to our continued interest in organocatalysis,<sup>3</sup> we investigated the significance of these intermediates in stereocontrolling step in proline catalyzed reactions. Our results which aid in unraveling the correct TS model (a, b or c) will be the focus of presentation.<sup>4</sup>



Enamine Carboxylic Acid Model (a)



Enamine Carboxylate Model (b)



Oxazolidinone Model (c)

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