

Allenyl ester building blocks: α -Selective reactions leading to products containing all-carbon quaternary centers

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We are currently developing a program to exploit allenyl esters as building blocks in complex small-molecule synthesis. In this vein, we have discovered that a wide variety of electrophiles can be added to the α -position of allenates following a mechanism involving an initial attack at the allene sp -carbon to create a nucleophilic species.



In this presentation, we describe how catalytic alkoxides under biphasic conditions promote the reaction of silyl allenates ($R = \text{SiEt}_3$) with a variety of carbon electrophiles to afford all-carbon quaternary centers bearing an ethynyl group. Although this alkoxide-catalyzed reaction adds to an exceptionally broad range of electrophiles including aryl fluorides (via S_NAr), it does not add aldehydes at the α -position of allenates to afford β -hydroxy esters. As a solution to this shortcoming, we will describe a titanium-mediated addition of achiral allenates ($R = H$) that adds aldehydes to the desired position leading to products bearing an all-carbon quaternary center with complete *anti* diastereoselectivity. Trisubstituted allenates led to products in which the resulting alkene was obtained as the *Z*-isomer leading to unprecedented triple diastereoselectivity. The role of TiX_4 reagents to bring about an ordered bimolecular addition of allenates and aldehydes affording the observed α -selective results will also be discussed. To our knowledge, this is the first time both the α -quaternary and the β -carbinol centers are installed simultaneously with complete diastereoselectivity. Details relating to optimization of both reactions and current attempts and prospects for rendering these reactions asymmetric will also be presented.

