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Stereoselective Synthesis of Trisubstituted Olefins

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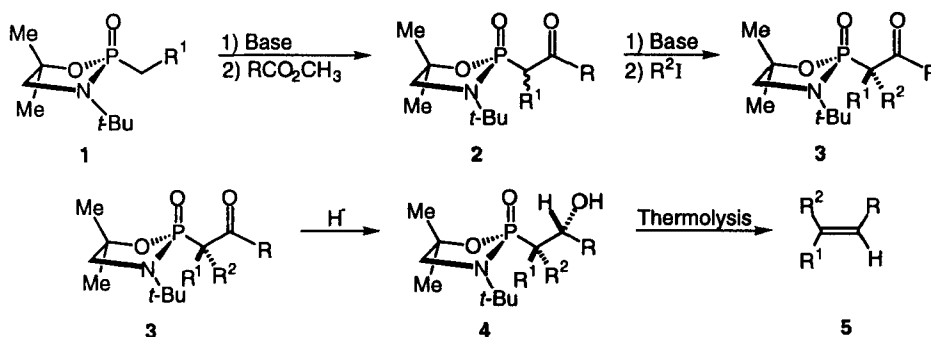
STERESELECTIVE SYNTHESIS OF TRISUBSTITUTED OLEFINS

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A new method for the highly stereoselective synthesis of trisubstituted olefins is presented. The method involves the stereoselective construction of various β -hydroxy phosphonamidates followed by their thermolysis to provide trisubstituted olefins in extremely high geometrical purity (>99/1).

The stereoselective construction of β -hydroxy phosphonamidates could be accomplished through three main synthetic transformations. The first involves the acylation of various parent 1,3,2-oxazaphospholidines (**1**) to provide monoalkylated β -keto phosphonamidates (**2**) in good yield. The second step is the alkylation of the β -keto phosphonamidates to provide α,α -dialkylated β -keto phosphonamidates (**3**) in high yield and very high diastereoselectivities. Finally, the highly diastereoselective reduction of the dialkylated β -keto phosphonamidates could be accomplished through the use of a variety of reducing agents to give β -hydroxy phosphonamidates (**4**) in high yield and high diastereoselectivities.



Thermolysis of the diastereomerically pure β -hydroxy phosphonamidates gave a variety of trisubstituted olefins (**5**) in high yield and stereoselectivity. This methodology has also been applied towards the stereoselective synthesis of tetrasubstituted olefins.

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