Asymmetric Syntheses of Unsaturated Amino Acids and Peptides via Chelate-Enolate Claisen Rearrangements

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_N_-protected amino acid allylic esters can easily be deprotonated by LDA at -78 °C and transmetallated by addition of metal salts. Chelated metal enolates, which undergo Claisen rearrangements upon warming up to room temperature, giving rise to unsaturated amino acids, are formed with many different salts. Due to the fixed enolate geometry as a result of chelate formation, the rearrangement proceeds with a high degree of diastereoselectivity. This procedure can be applied to acyclic as well as to cyclic substrates and allows for the synthesis of amino acids containing quarternary carbon centers. Starting from chiral allylic alcohols, optically active amino acids are obtained. This chirality transfer can also be used for stereoselective peptide modifications. If tosylated peptide allylic esters are subjected towards Claisen rearrangement, the chirality of the peptide chain can also be used as a stereocontrolling element. Another possibility to introduce chirality is given by the rearrangement in the presence of chiral ligands. Best results so far are obtained if Al(OiPr)_3 is used as the chelating metal salt and the Chinchona alkaloids as bidentate ligands. Quinine gives rise to (2R)-configured amino acids, while quinidine delivers the (2S) derivatives in very high yields and excellent enantioselectivities (80 - 93% ee). Therefore this protocol can easily be applied to natural product synthesis.