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Chiral Vinyl Sulfoxides as Useful Reagents for the Synthesis of β -Amino Acid Derivatives

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(*S*)- and (*R*)- β -amino acid derivatives were synthesized by the asymmetric conjugate addition of ammonia and piperidazine to *t*-butyl (*E*)-2-[(*R*)- and (*S*)-*p*-tolylsulfinyl]cinnamates, respectively.

KEY WORDS: CHIRAL VINYL SULFOXIDES; CONJUGATE ADDITION;
 β -AMINO ACID DERIVATIVES; (*S*)-CELACINNINE

INTRODUCTION

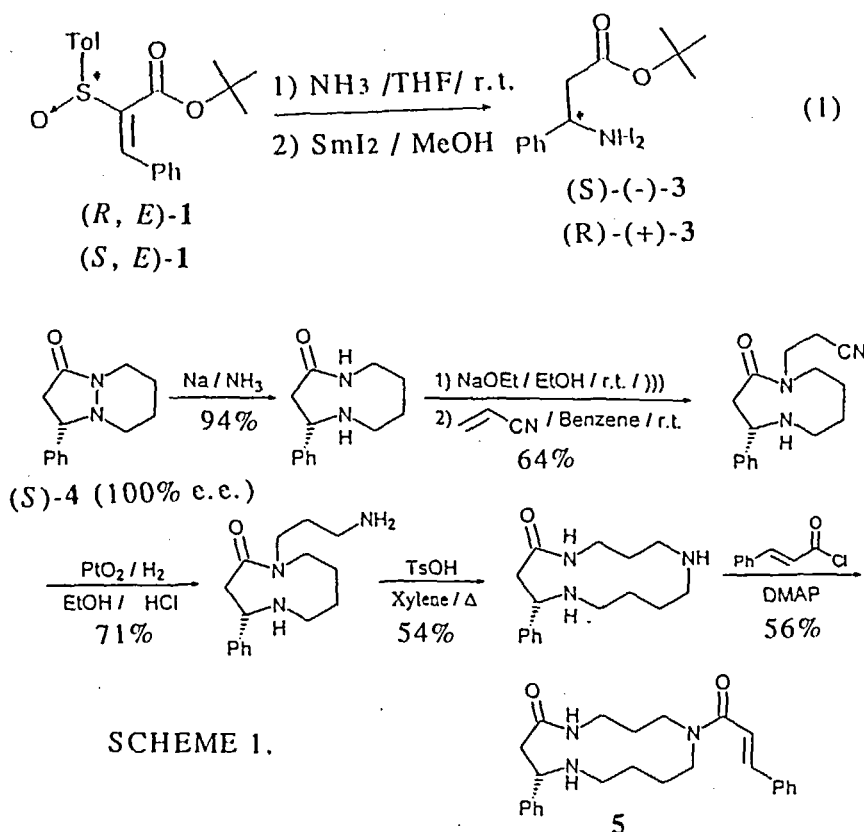
Many classes of natural products contain β -amino acid derivatives as fragments. For example, β -phenylalanine derivatives are constituents of many of the polyamine alkaloids, which are antibiotics and antihypertensive.¹

SYNTHESIS OF β -AMINO ACID DERIVATIVES

Recently, enantiomerically pure vinyl sulfoxides have proved to be useful reagents in stereoselective synthesis.² Our synthetic approach to β -amino acid derivatives is outlined in Equation 1. The conjugate addition of ammonia to chiral vinyl sulfoxides³ (*R*)-**1** and (*S*)-**1**, followed by successive reduction of *p*-tolylsulfinyl group of the adducts **2** with SmI_2 proceeded smoothly at room temperature in THF to give (*S*)-(-)- and (*R*)-(+)-*t*-butyl β -amino- β -phenylpropionates (**3**) in 68% yield with good optical purity (74 and 81% e.e.), respectively. In the reactions of (*R*)-**1** and (*S*)-**1** with benzylamine in THF at room temperature, the stereoselectivity was moderate (52% e.e.).

SYNTHESIS OF (*S*)-(-)-CELACINNINE

In the reactions of (*R*)-1 and (*S*)-1 with six-membered hydrazine, piperidine, in the presence of potassium *t*-butoxide in THF at room temperature, the conjugate addition-cyclization proceeded stereoselectively and (*S*)-4 and (*R*)-4 were obtained in 73 and 75% yields with high enantiomeric purity (95% e.e.), respectively. The bicyclic compound 4 is a key intermediate in the total synthesis of natural thirteen-membered polyamine alkaloids,¹ celacinnine and *N*(1)-acetyl-*N*(1)-deoxymayfoline, and the first synthesis of (*S*)-(-)-celacinnin (5) $[\alpha]_D -16.5^\circ$ (*c* 0.10, CHCl₃); natural celacinnine³ $[\alpha]_D -19^\circ$ (*c* 0.16, CHCl₃) was accomplished by the ring-expansion method starting from (*S*)-(-)-4 (100% e.e.) (Scheme 1).



SCHEME 1.

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