[PD1-23] [2003-10-10 14:00 - 17:30 / Grand Ballroom Pre-function]

Preparation of Enantiomerically Pure Chiral builing block ((E)-4-(tributylstannanyl) but-3-en-2-ol) via lipase-mediated resolution

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Chiral building blocks have the importance in the pharmaceutical and agrochemical industries as well as in the development of rapid and efficient syntheses of bioactive compounds and natural product. Vinylstannane contains two synthetically useful functional groups (vinylstannane and allylic alcohol). The vinylstannane functional group can be used in C-C bond formation under a variety of conditions and the allylic alcohol functional can be used in hydroxyl-directed epoxidations, cyclopropanations, and sigmatropic rearrangements. We have been able to obtain enantiomerically pure (E)-4-(tributylstannanyl)but-3-en-2-ol by kinetic enzymatic resolution using a cheap and commercially available lipozyme.

[PD1-24] [2003-10-10 14:00 - 17:30 / Grand Ballroom Pre-function]

Stereoselective Total Synthesis of (-)-Cytoxazone

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We have developed the novel one-pot synthetic method for regioselective and stereoselective N-protected amines through the reaction of various ethers with chlorosulfonyl isocyanate (CSI). Also, we found a novel technique to compare directly the stability of carbocations in the solution phase and established the stability order of the various carbocations. And we reported the cleavage of benzyl and p-methoxybenzyl protecting groups of alcohols and phenols in the presence of other functional groups using CSI. Also, we established that our CSI reaction is a competitive reaction of S_Ni and S_N1 reaction according to the stability of carbocation intermediate. Now, we report a stereoselective total synthesis of the (-)-cytoxazone, a novel 4,5-disubstituted-2-oxazolidinone compound isolated from Streptomyces species has shown cytokine modulating activity, base on the regioselective and stereoselective CSI reaction we develope. The total synthesis of (-)-cytoxazone was achieved in 6 linear steps from p-anisaldehyde. Key steps in this route are the regioselective and stereoselective introduction of N-protected amine group using our CSI reaction of anti-1,2-dimethyl ether and the subsequent regioselective cyclization of N-protected amino diol to give the 2-oxazolidinone unit of (-)-cytoxazone. We also found the optimum reaction conditions for the diastereoselective CSI reaction of anti- and syn-1,2-dimethyl ethers. The retention of configuration can be explained by the neighboring group effect. This synthetic method using CSI can be applied to the formation of various natural products with a more complex amine.

[PD1-25] [2003-10-10 14:00 - 17:30 / Grand Ballroom Pre-function]

Studies Toward the Total Synthesis of Perhydrohistrionicotoxin

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Natural histrionicotoxin, a substance isolated from the skins of the "arrow poison frog" and its fully hydrogenated derivative, perhydrohistrionicotoxin (pHTX), have been the subject of synthetic investigation because of their important neurophysiological activity and a unique framework. In this work, we could obtained the appropriately functionalized spiropiperidine compound as a formal precursor of perhydrohistrionicotoxin. An important feature of this synthesis is the creation of a stereogenic center by using Ireland-Claisen Rearrangement, and Ring-Closing Metathesis (RCM).