Selenium Mediated Cyclizations and Reactions of Selenones

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Abstract

An investigation of stereoselective selenium mediated cyclizations of allylic alcohols was carried out. Cyclizations of N-protected 4-hydroxy-5-pentenylamines occurred under kinetic control with cis-stereoselectivity to afford N-protected phenylselenomethyl hydroxypyrrolidines in high yield. Selenium induced cyclizations of N-protected 3-hydroxy-6-hexenylamines occurred under thermodynamic control with trans-stereoselectivity to afford N-protected phenylselenomethyl hydroxypipеридines in high yield. A mechanism to account for these contrasting reactivities is proposed. Some of the piperidines formed stable hydrates and exhibited through space coupling to water in the $^{1}$H n.m.r. spectra. Some of the pyrrolidines were elaborated to biologically important diols via intramolecular substitution of the corresponding selenones with hydroxide ion.

The conditions required for formation of alkyl phenyl selenones from alkyl phenyl selenides using MCPBA were investigated using $^{77}$Se n.m.r. analysis. Several intermolecular substitution reactions of alkyl phenyl selenones by soft nucleophiles such as water, methanol and chloride ion were demonstrated to occur under mild conditions and in high yield. Treatment of β-benzamidodiselenides with MCPBA and base at room temperature afforded cis-fused 2-oxazolines, whereas treatment with excess phenylselenenyl bromide at 120°C afforded previously unreported trans-fused 2-oxazolines. Treatment of β-acetamidodiselenides with MCPBA gave lactones or esters.

Hydroxyselelenations of allylic alcohols generally occurred with high regioselectivity to afford β,β′-dihydroxyselelenides, which could be transformed to β-hydroxy epoxides upon treatment with MCPBA and base. The formation of trans-β-hydroxy epoxides from allylic alcohols using this methodology is in contrast to established methods which give cis-β-hydroxy epoxides.

Hydroxyselelenation of crotyl acetate or 2-acetoxy cyclohexene was regio- and stereo-catholic, in contrast to the regio- and stereo-specific addition of phenylselenenyl chloride to these compounds. Additions of phenylselenenyl chloride in the presence of zinc chloride to these compounds was also regio- and stereo-catholic. A mechanism to account for these differing reactivities is proposed.

Attempts to induce radical, reductive or oxidative cyclizations of N-acryloyl and N-alkyl 2-phenylselenomethyl pyrrolidines were unsuccessful, however N-acrylated or N-alkylated β-amidodiselenides could be cyclized to form five and six membered ring nitrogen heterocycles via radical abstraction of selenium.