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[Lab. of Pharm. Chemistry]

Meyer-Schuster Rearrangement of γ -Sulfur-substituted Propargyl Alcohols: A Convenient Synthesis of α , β -Unsaturated Thioesters

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 γ -Sulfur-substituted propargyl alcohols reacted with polyphosphoric acid trimethylsilyl ester (PPSE) to give the α , β -unsaturated thioesters in good yields. However the reactions of 3,3-dibutyl-1-(phenylthio)propargyl alcohol and 1-(phenylthio)ethynyl-1-cycloalkanols with PPSE gave the enyne sulfides exclusively. The mechanism for formation of the α , β -unsaturated thioesters and the enyne sulfides is discussed.

[Tetrahedron Lett., **36**, 5559 - 5562 (1995)]

[Lab. of Pharm. Chemistry]

Ring Transformation of 1,2-Thiazetidine 1,1-Dioxides with Lewis Acids: Formation of *trans*-1,2,3-Oxathiazolidine 2-Oxides and *cis*-Aziridines

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Treatment of 1,2-thiazetidine 1,1-dioxides (β -sultams) bearing a poor migratory substituent at C-3 with Lewis acids such as EtAlCl₂ and AlCl₃ provided *trans*-1,2,3-oxathiazolidine 2-oxides and/or *cis*-aziridines *via* the C-S bond cleavage and recyclization. *cis*-Aziridines and/or ketones were provided from the reactions of 3-aryl- β -sultams with SnCl₄, depending on the migratory aptitude of the C-3 aryl substituent and configuration of C-3 and C-4 groups. Hydrolysis of $(2R^*,4S^*,5S^*)$ -3-cyclohexyl-5-phenyl-4-(3-pyridyl)-1,2,3-oxathiazolidine 2-oxide with 1N HCl-THF provided $(1S^*,2S^*)$ -2-aminoethanol derivative in 84% yield together with a small amount of $(1R^*,2S^*)$ -isomer.

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[Lab. of Pharm. Chemistry]

A Useful Synthesis of α , β -Bis(methylseleno)alkanes and α , δ -Bis(methylseleno)alk-2-enes by the Reactions of Alkenes and 1,3-Dienes with B(SeMe)₃-Lewis Acid

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Reactions of tris(methylseleno)borane-SnCl₄ with alkenes gave α , β -bis(methylseleno)alkanes stereospecifically, and reactions with 1,3-dienes afforded α , δ -bis(methylseleno)alk-2-enes regioselectively. 1,4-Methylseleno groups of 1,4-bis(methylseleno)alk-2-enes could be changed to other functional groups. The methylation reaction of 1,4-bis(methylseleno)-2,3-diphenylbut-2-ene with various bases and MeI gave 2,3-diphenylbut-1,3-diene, and the reaction with NBS afforded 1,4-dibromo-2,3-diphenylbut-2-ene.