

[Tetrahedron Lett., 37, 2257-2260 (1996)]

[Lab. of Pharm. Chemistry]

**Selective C-N Bond Cleavage of 4-Silyl-substituted 1,2-Thiazetidines,
1,1-Dioxides with EtAlCl₂: Stereospecific Formation of (*E*)-
Vinylsulfonamides.**

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Monosilylation of 4-non-substituted β -sultams was achieved by use of *t*-butyldimethylsilyl chloride as a silylating reagent to give (3*R**,4*S**)-4-silylated β -sultams stereoselectively. Silylation of 4-substituted β -sultams also proceeded stereoselectively. 4,4-Disilylated β -sultams were obtained from reactions of 4-non-substituted β -sultams with trimethylsilyl chloride. Treatment of 4-silylated β -sultams with a Lewis acid caused the selective C-N bond cleavage because of the β -silyl stabilization against the resultant carbenium ion followed by desilylation to provide (*E*)-vinylsulfonamides stereospecifically.

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[Lab. of Pharm. Chemistry]

**Reinvestigation of Reactions of Thiazolium and Benzothiazolium *N*-
Phenacylides with Electron-deficient Acetylenes.**

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The thiazolium *N*-phenacylides, generated *in situ* from 4-methyl- or 5-phenyl-3-phenacylthiazolium bromide with triethylamine, reacted with dimethyl acetylenedicarboxylate (DMAD) in dry DMF to give the thiazole ring-opened products, in which two molecules of DMAD had been incorporated. The reactions when conducted both in aqueous DMF and in dry DMF in the presence of lithium perchlorate gave the hemiacetals which could be transformed into the 1:2 reaction products of the ylides and DMAD. Benzothiazolium *N*-phenacylides similarly reacted with DMAD to afford the 1:2 reaction products or the hemiacetals.

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**Synthesis and Characterization of Bis[1.1.1]orthocyclophano-18-
crown-6 Compounds.**

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Two novel macrocyclic compounds 5S and 5A combining an 18-crown-6 and two cyclotrimeratrylenes were synthesized by means of two methods from dibenzo-18-crown-6. The conformational isomers were separated using complexation with KSCN and their stereostructures were determined on the basis of ¹H-NMR spectroscopic and thermal equilibration studies. The function of isomer 5S was investigated by the use of several organic compounds (C₆₀, anthraquinone, etc.) under various conditions. Contrary to our expectation, however, no inclusion was observed.