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[Lab. of Pharm. Chemistry]

The Chalcogeno-Baylis-Hillman Reaction: The First Examples Catalysed by Chalcogenides in the Presence of Lewis Acids.

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The chalcogeno-Baylis-Hillman reaction catalyzed by sulfides and selenides, the group 16 element compounds, in the presence of Lewis acids was developed. The reactions proceeded smoothly by the use of 1 equiv. of TiCl_4 to give the coupling products in moderate to good yields even for only 1 h at room temperature. Bis-chalcogenides and related compounds were investigated as a catalyst, and 1,5-diselenocyclooctane gave the best result owing to stabilization of a cationic intermediate by the transannular interaction.

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Reactions of 1,2-Thiazetidene 1,1-Dioxides with Organometallics: β -Elimination and N-S Bond Cleavage.

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Reactions of 4-nonsubstituted β -sultams with methyllithium gave only (*E*)-vinylsulfonamides, whereas 2-aminoethyl sulfones were obtained as minor products by use of methylmagnesium bromide. Reactions of 4-monosubstituted β -sultams with organolithiums gave (*E*)-vinylsulfonamides stereoselectively regardless of the configuration of 3- and 4-substituents. Treatment of a 4,4-dimethyl- β -sultam with methylmagnesium bromide and methyllithium provided a 2-aminoethyl sulfone and a bis-sulfone, respectively, and isopropyl phenyl sulfone was obtained by use of phenyllithium or phenylmagnesium bromide.

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Reactions of a β -Sultam Ring with Lewis Acids via the C-S Bond Cleavage.

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Selective C-S bond cleavage of a β -sultam ring was achieved by the reactions with Lewis acids. Aryl ketones or aldehydes were provided from 3-aryl- β -sultams whereas β -sultams bearing a poorly migratory substituent at C-3 gave *trans*-1,2,3-oxathiazolidine 2-oxides and/or *cis*-aziridines. These reactions were influenced by the cation-stabilizing capability of C-4 substituents and by the configuration of the substituents at C-3 and C-4. A (*1R**,*2R**)-2-aminoethanol derivative was obtained by hydrolysis of a *trans*-1,2,3-oxathiazolidine 2-oxide. Some 4-alkenyl-3-aryl- β -sultams underwent tandem intramolecular cyclization to give bicyclo[3.2.1]- and [2.2.1]- γ -sultams via the processes of C-S bond cleavage, 1,2-aryl shift, cation-olefin cyclization and recombination of the sulfonyl anion.

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The Chalcogeno-Baylis-Hillman Reaction: A New Preparation of Allylic Alcohols from Aldehydes and Electron-deficient Alkenes.

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The chalcogeno-Baylis-Hillman reaction was investigated by the use of chalcogenides as catalysts in the presence of Lewis acids. The reaction was applied to activated alkenes such as enones including β -substituted derivatives, acrylonitrile, methyl acrylate and phenyl vinyl sulfone. Diethyl vinylphosphonate and phenyl vinyl sulfoxide were inactive to the chalcogeno-Baylis-Hillman reaction. 1,5-Diselenocyclooctane gave the best result as a catalyst due to the transannular interaction between the selenium atoms. TiCl_4 was the best Lewis acid, and 1 equiv. of TiCl_4 was necessary for smooth reactions.