Novel Construction of 5-Methylenepyrrol-2-ones by Intramolecular Cyclization of Selenium-Stabilized Alkynyl Amides.

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S-Ethyl 3-ethoxy-5-(phenylchalcogeno)pent-4-ynethioates were prepared by an α-site-selective reaction of γ-chalcogen-substituted prop-2-ynyl cations with S-ethyl O-silyl enol ethers. These thioesters were treated with amines to give the alkynyl amides in moderate yields. The alkynyl amides reacted with t-BuOK-t-BuOH in the presence of 18-crown-6 to give (Z)-5-(phenylselenomethylene)pyrrol-2-ones in good yields. Isomerization of the (E)- and (Z)-alkenyl groups of the pyrrolones was observed under acidic conditions. Cycloaddition of a pyrrol-2-one and diazomethane gave regioselectively a pyrazole the subsequent denitrogenation of which gave cyclopropane derivative in good yield.

Stereospecific Syntheses of 5-Alkyl-3-ethoxy-2-
[(phenylchalcogeno)methylene]tetrahydrofurans.

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2-Ethoxy-4-(phenylchalcogeno)but-3-ynyl ketones were reduced with lithium borohydride in ether diastereoselectively to give 5-(phenylchalcogeno)pent-4-yn-1-ols. Treatment of the phenylchalcogen-substituted alkynyl alcohols with t-BuOK in t-BuOH provided useful (Z)-2-
[(phenylchalcogeno)methylene]tetrahydrofurans stereoselectively. The novel cyclization described in this paper proceeds via intramolecular oxymetalation of the acetylenic moiety of the alkynyl alcohol substrates.

Separation of Racemic and Meso-1,2-bis[2-[2-(bromo-4,5-
dimethoxyphenyl)hydroxymethyl]-4,5-dimethoxybenzyl]-4,5-
dimethoxybenzenes by Host-guest Inclusion.

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A dilithiolide, derived from 1,2-bis(2-bromo-4,5-dimethoxybenzyl)-4,5-dimethoxybenzene and n-BuLi, reacted with 2.1eq. of 6-bromoveratraldehyde to give diastereoisomers of title compounds in 73% yield. Recrystallization of the mixture from AcOEt-hexane furnished one isomer as 1:1 adduct with AcOEt. On the other hand, the residue was recrystallized from EtO-acetone to afford another isomer as 1:1 complex with EtO. Their stereostructures were determined by 1H-NMR measurement using a chiral shift reagent, Eu(tfc).