[J. Chem. Soc., Perkin Trans. 1, 1839-1843 (1996)]

[Lab. of Pharm. Chemistry]

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

Mitsuhiro Yoshimatsu, Keigo Machida, Takayo Fuseya, Hiroshi Shimizu, Tadashi Kataoka*

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.

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[Lab. of Pharm. Chemistry]

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

Mitsuhiro Yoshimatsu, Motoyo Naito, Hiroshi Shimizu, Osamu Muraoka, Genzo Tanabe, Tadashi Kataoka*

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.

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[Lab. of Pharm. Chemistry]

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.

Hiroshi Hara, Hiroshi Nakamura, Shin-ichi Watanabe*,

TOMOMI MURATA, OSAMU HOSHINO

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 Et₂O-acetone to afford another isomer as 1:1 complex with Et₂O. Their stereostructures were determined by ¹H-NMR measurement using a chiral shift reagent, Eu(tfc)₃.