

[Tetrahedron Lett., 32, 105-108 (1991)]

[Lab. of Pharm. Chemistry]

**Endo Selective Cyclization of Selenonium Ion Intermediate: Efficient Formation of 1-Halo-3-selenocyclohexanes.**

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Selenoacetals were synthesized in satisfactory yields by two methods: one is selenoacetalization of aldehydes or ketones using tris(methylseleno)borane and a catalytic amount of trifluoroacetic acid, and the other is alkylation of bis(phenylseleno)methane. One of the C-Se bonds of selenoacetals was cleaved with tin (IV) or titanium (IV) halides and the selenonium ion intermediates ( $\alpha$ -seleno carbocations) were generated *in situ*. Olefinic selenoacetals were cyclized with tin (VI) chloride in the 6-Endo-Trig mode to give 1-chloro-3-methylselenocyclohexanes regio- and stereoselectively. Bromo- or iodocyclohexane derivatives were afforded by use of tin (IV) bromide or titanium (IV) iodide, respectively.

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[Lab. of Pharm. Chemistry]

**Reactions of Azathiabenzene Anion with Electrophiles. Formation and X-Ray Analysis of Novel Heterocyclic Compounds from the Reaction with Carboxylic Esters.**

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The reactivity of the methyllide (1) generated from 9-methyl-10-aza-9-thiaphenanthrene by treatment with LDA was investigated. The methyllide (1) was allowed to react with trimethylsilyl chloride to afford ring-expanded product, benzothiazepine derivative. On the contrary, treatment of (1) with carboxylic esters resulted in the formation of ring-contracted products, dihydro[1]benzothieno[2,3-*c*]indol derivatives, *via* Sommelet-Hauser rearrangement, whose structures have been confirmed by an X-ray crystal structure determination.

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**A Polar Cycloaddition of 2-Thianaphthylum Ions with 1,3-Dienes and Some Properties of the Cycloadducts.**

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2-Thianaphthylum salts (1) underwent a polar cycloaddition with 1,3-dienes to afford benzo-fused bicyclic sulfonium salts (2) bearing sulfur atom at the bridge-head in excellent yield. The cycloadducts underwent retro-addition reaction to generate the cation (1), which was easily trapped with other diene or acetone. Reactions of the adducts (2) with several nucleophiles caused the ring-opening of (2) to afford 1-allyl- and 1-homoallyl substituted 2-thiochromenes in good yields.