

[Tetrahedron Lett., 31, 115 (1990)]

First Isolation of Monocyclic Thiabenzenes.

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Monocyclic thiabenzenes, 1-alkyl-2-aryl-(or 1-alkyl-2-cyano-)4,5-dimethylthiabenzenes (2) were successfully synthesized by deprotonation of the corresponding thiopyranium salts (1) with triethylamine in ethanol. The thiopyranium salts (1) were synthesized as follows. Dihydrothiopyrans prepared by Diels-Alder reaction of 1,3-butadiene derivatives with thioaldehydes were led to the sulfoxides by *m*-CPBA oxidation. The sulfoxides were submitted to the dehydration conditions to give the corresponding 6*H*-thiopyrans, which were alkylated to afford the corresponding thiopyranium salts (1). The ylidic nature of (2) was elucidated by spectral and chemical evidence. Thermal reaction of (2) in several solvents provided S-alkyl rearranged products and ring-contracted ones, depending upon solvents used.

[Tetrahedron Lett., 31, 3027 (1990)]

Novel Synthesis of Medium-sized Heterocycles Containing a Sulfur or Selenium Atom.

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Medium-sized sulfur- or selenium-containing heterocyclic compounds were synthesized by the reductive cross-piece bond cleavage of bicyclic sulfonium and selenonium salts bearing a bridgehead sulfur or selenium atom with magnesium metal or sodium borohydride. Selenonium salts were reduced more easily than the corresponding sulfonium salts.

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Vinyl Radical Generation with Selenoborane and Its Application to Cyclization Reaction of Enynes.

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Tris(methylseleno)- and tris(phenylseleno) boranes added to acetylenes to afford methylseleno- and phenylseleno-substituted (*Z*)-vinylselenides in high yields. The addition reactions proceeded by way of free radicals and were applied to cyclization reactions of enyne compounds. The radical cyclization provided pyrrolidine derivatives diastereoselectively.