First Isolation of Monocyclic Thiabenzenes.

HIROSHI SHIMIZU, NORIAKI KUDO, TADASHI KATAOKA, MIKIO HORI*

Monocyclic thiabenzenes, 1-alkyl-2-aroyl-(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.

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

TADASHI KATAOKA, KAZUHIRO TSUTSUMI, TETSUO IWAMA,

HIROSHI SHIMIZU, MIKIO HORI*

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.

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

TADASHI KATAOKA, MITSUHIRO YOSHIMATSU, HIROSHI SHIMIZU,

MIKIO HORI*

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.