

## SYNTHETIC APPROACH TO MONOCYCLIC 1,4-THIAZEPINES

Shoko Yamazaki, Hiroki Osedo, Kagetoshi Yamamoto, and Ichiro Murata  
 Department of Chemistry, Faculty of Science, Osaka University, Toyonaka,  
 Osaka 560, Japan

Yoshimasa Fukazawa  
 Department of Chemistry, Faculty of Science, Hiroshima University,  
 Naka-ku, Hiroshima 730, Japan

Monocyclic 1,4-thiazepines are the class of synthetically inaccessible heteropines which liberate readily sulfur atom to give the corresponding aromatic compounds. We have recently demonstrated that the monocyclic thiepinines belonging to those heteropines are stabilized by two t-butyl groups at C<sub>2</sub> and C<sub>7</sub>. As part of our continuous studies on these heteropines, we have succeeded in the first synthesis of an isolable monocyclic 1,4-thiazepine derivative, keeping the above stabilizing effect in mind.

The first subgoal was the synthesis of thiapyranone (3) which could not be obtained by the conventional ring-closure methods. The thiopyrylium ion (1), prepared from thiophene in five-steps according to the procedures developed by us, was oxidized with CrO<sub>3</sub>-pyridine to give 2 in 56 % yield. Reduction of 2 with NaBH<sub>4</sub> and subsequent oxidation of the initial product with CrO<sub>3</sub>-pyridine furnished 3 in 52 % overall yield from 2.

Ketone (3) was converted to the key seven-membered intermediate (4) in three-steps involving Beckmann rearrangement reaction. Introduction of an additional double bond required for the synthesis was accomplished by the Pummerer reaction procedure to give 5, reaction of which with Me<sub>3</sub>O<sup>+</sup>BF<sub>4</sub><sup>-</sup> proceeded smoothly with formation of the final product (6).

