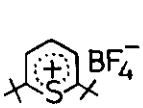
SYNTHETIC APPROACH TO MONOCYCLIC 1,4-THIAZEPINES

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 Univeristy, Naka-ku, Hiroshima 730, Japan

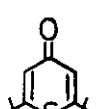
Monocyclic 1,4-thiazepines are the class of synthetically inaccessible heteropines which liberate readily sulfur atom to give the corresponding aromatic compounds. We have recently demonstrated that the monocyclic thiepines belonging to those heteropines are stabilized by two t-butyl groups at C_2 and C_7. 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_3-pyridine to give 2 in 56 % yield. Reduction of 2 with $NaBH_4$ and subsequent oxidation of the initial product with CrO_3-pyridine furnished 3 in 52 % overall yield from 2.

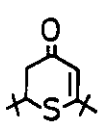
Ketone (3) was converted to the key seven-membered intermediate (4) in three-steps involving Beckmann rearrangement reaction. Introduction of an additional double bond required for the synthesis was accomplished by the Pummerer reaction procedure to give 5, reaction of which with $Me_3O^+BF_4^-$ proceeded smoothly with formation of the final product (6).



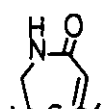
1



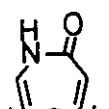
2



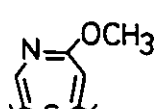
3



4



5



6