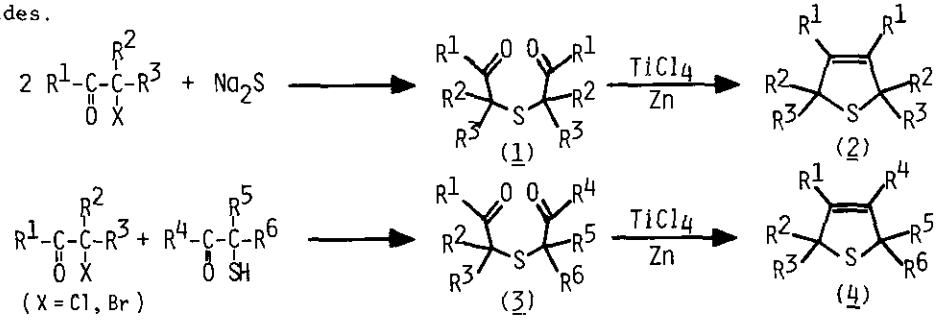
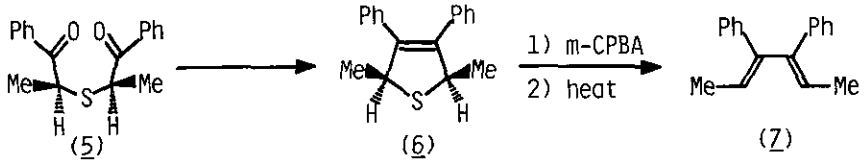
GENERAL SYNTHESIS AND SYNTHETIC APPLICATION OF 2,5-DIHYDROTHIOPHENES

Haruki Machida, Juzo Nakayama, and Masamatsu Hoshino
Department of Chemistry, Faculty of Science, Saitama University,
Urawa, Saitama 338, Japan

Diketo sulfides (1) are easily prepared from α-haloketones and sodium sulfide. Reduction of (1) by low valent titanium prepared from $TiCl_4$ and Zn gave a wide variety of symmetrically substituted 2,5-dihydrothiophenes (2) in good yields. In a similar way, unsymmetrically substituted 2,5-dihydrothiophenes (4) are also prepared from diketo sulfides (3) which are obtainable from α-halo- and α-mercapto-sulfides.



Oxidation of (1) by m-CPBA followed by thermolysis of the resulting sulfones furnished a variety of 1,3-dienes in good overall yields. Reduction of the meso-sulfide (5) afforded the cis-dihydrothiophene (6) stereospecifically. Oxidation of (6) and subsequent thermolysis of the resulting sulfone gave the 1,3-diene (7) in a stereospecific manner.



When reduction of (1) were done under the controlled conditions, 3,4-dihydrothiolanes (8) were obtained in good yields.