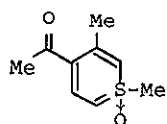


STRUCTURES AND REACTIVITIES OF 4-ACYL-1-METHYLTHIABENZENE 1-OXIDES
AND THE 2-AZA DERIVATIVES

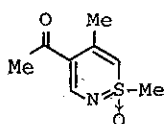
Yasumitsu Tamura, Masayoshi Tsunekawa, Hiroshi Taniguchi, Tomohisa Miyamoto,
Masazumi Ikeda, Takaji Fujiwara, Toshiyasu Hombo, and Ken-ichi Tomita
Faculty of Pharmaceutical Sciences, Osaka University, 133-1,
Yamada-kami, Suita, Osaka, Japan

4-Acyl-1-methylthiabenzene 1-oxides (1) have been prepared by the reaction of 3-ethoxymethylene-2,4-pentanedione (2), ethyl 2-(ethoxymethylene)acetoacetate (3), and 2-acetyl-3-methoxy-2-cyclohexen-1-one (4) with dimethyloxosulfonium methylide. 4-Acyl-1-methyl-2-thiabenzene 1-oxides (5) have been synthesized by base-catalyzed cyclization of N-(β,β -diacylvinyl)dimethylsulfoximines which, in turn, were obtained by the reactions of (2)-(5) with dimethylsulfoximine.

Spectral (ir, uv, $^1\text{Hnmr}$, and $^{13}\text{Cnmr}$) and chemical (deuterium exchange, bromination, and NaBH_4 reduction) properties of (1) and (6) suggest that both (1) and (6) are best represented by cyclic ylidic structures, but the ylidic and betaine-like properties of (6) are much lower than those of (1). These conclusions were further substantiated by X-ray single-crystal structure analyses of 4-acetyl-1,3-dimethylthiabenzene 1-oxide (1a) and 4-acetyl-1,5-dimethyl-2-azathiabenzene 1-oxide (6a).



(1a)



(6a)