

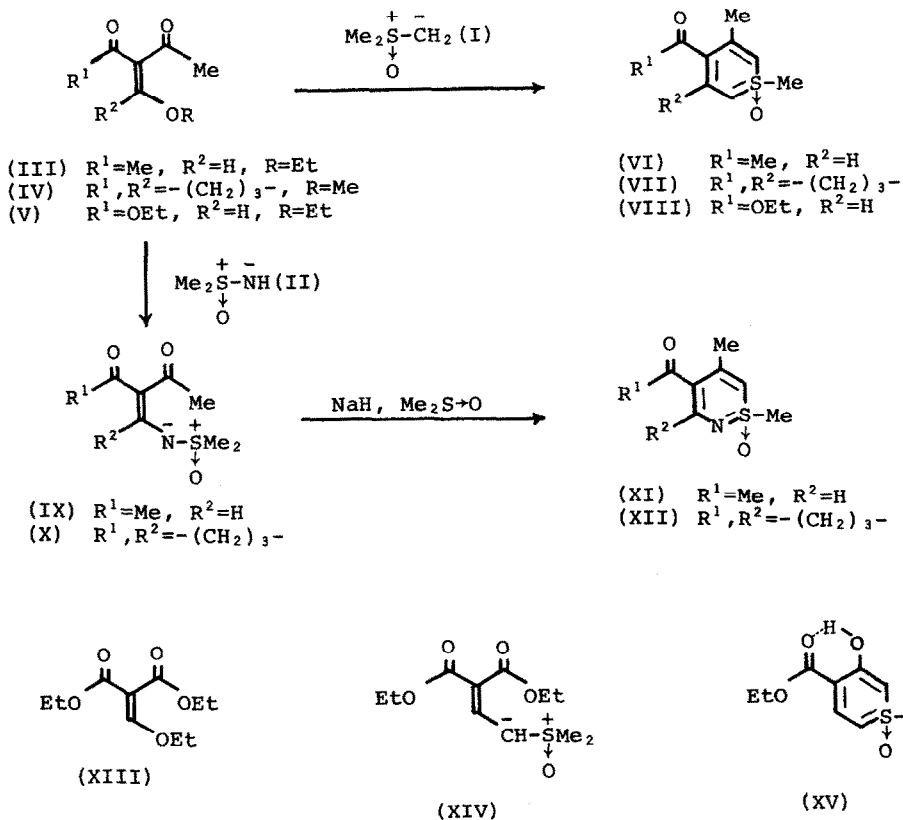
SYNTHESES OF 4-ACYL-1-METHYLTHIABENZENE 1-OXIDES  
AND THEIR 2-AZA ANALOGS

Y. Tamura, T. Miyamoto, H. Taniguchi, K. Sumoto, and M. Ikeda  
Faculty of Pharmaceutical Sciences, Osaka University  
Toneyama, Toyonaka, Osaka, Japan

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The chemistry of thiabenzene 1-oxide and its aza analogs is of substantial intrinsic interest as one of heterocycles containing six  $\pi$ -electrons in the ring. Recently several synthetic methods for these compounds have been achieved.<sup>1-5</sup> One of the most commonly used methods involves the reaction of acylacetylenes and dimethyl sulfoxonium methylide (I)<sup>1,2</sup> or dimethyl sulfoximine (II).<sup>3</sup> We now wish to report a general method for 4-acyl-1-methylthiabenzene 1-oxides and their 2-aza analogs, which are new classes of derivatives of thiabenzene 1-oxides and not accessible by the known procedures. This method involves the use of 2,2-diacyl-1-alkoxyethylenes in place of acylacetylenes. In some cases, the intermediate 2,2-diacylvinyl-stabilized ylides or imines could be isolated.

Procedure 1: A solution of 3-ethoxymethylene-2,4-pentanedione<sup>6</sup> (III) (0.023 mole) in dimethyl sulfoxide (10 ml) was added to a solution containing I [prepared from trimethyl sulfoxonium iodide (0.046 mole) and sodium hydride (0.046 mole) in dimethyl sulfoxide (30 ml)]. The reaction mixture was stirred at room temperature for 2 hr, and then heated at 80-90° for 3 min. This was poured into ice water and extracted with chloroform. Evaporation of the solvent gave 4-acetyl-1,3-dimethylthiabenzene 1-oxide (VI),<sup>7</sup> mp 126.5-127°, as colorless crystals in 33% yield. In a similar manner, VII<sup>8</sup> was obtained from I and IV<sup>9</sup> in 29% yield. 4-Carboethoxy-1,3-dimethylthiabenzene 1-oxide (VIII), mp 92-92.5°, was also synthesized from I and V in 12% yield.

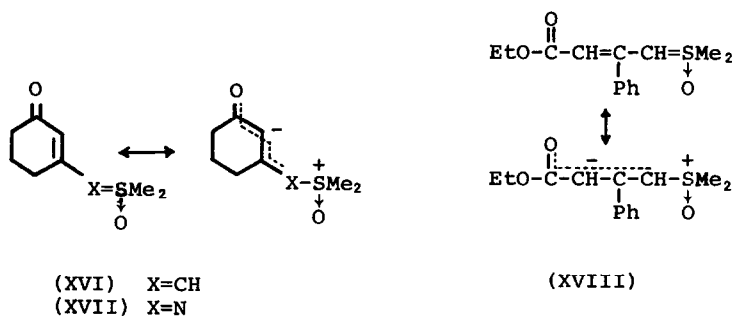


Procedure 2: Mixing III (0.02 mole) and II (0.02 mole) at room temperature followed by trituration with chloroform gave a new stabilized ylide IX, mp 164-165°, in 58% yield. Compound IX was treated with sodium hydride in dimethyl sulfoxide as described for VI to give XI, mp 94-95°, as colorless needles in 28% yield. Similarly reaction of II with IV afforded X, mp 126-126.5°, which, upon base treatment, cyclized to give XII, mp 97-97.5°, in 62% overall yield. Compound XV, mp 111-112°, was also obtained from I and XIII<sup>10</sup> via an intermediate XIV, mp 121.5-122.5°, in 13.5% overall yield.

As listed in Table, the infrared spectra of 4-acyl-1-methylthiabenzene 1-oxides and their 2-aza analogs (VI-VIII and XI-XII) showed relatively high-frequency carbonyl absorption bands by a comparison with the bands of compounds

Table N.m.r. chemical shifts ( $\tau$ ) of ring protons in  $\text{CDCl}_3$  and infrared carbonyl absorption bands ( $\text{cm}^{-1}$ ) of 4-acyl-1-methyl-thiabenzene 1-oxides and their 2-aza analogs

Compound	H-2	H-5	H-6	$\nu_{\text{max}}^{\text{CHCl}_3}$
VI	4.28-4.55	2.24	4.28-4.55	1641
VII	4.50 or 4.64	—	4.64 or 4.50	1632
VIII	4.22-4.58	2.00	4.22-4.58	1686
XI	—	1.74	4.20	1658
XII	—	—	4.26	1645
XV	4.81	2.26	4.57	1640



XVI<sup>11</sup> ( $\nu_{\text{max}}^{\text{CHCl}_3}$  1589  $\text{cm}^{-1}$ ), XVII<sup>12</sup> ( $\nu_{\text{max}}^{\text{CHCl}_3}$  1624  $\text{cm}^{-1}$ ), and XVIII<sup>2</sup> ( $\nu_{\text{max}}^{\text{Nujol}}$  1670  $\text{cm}^{-1}$ )

This suggests that the carbonyl groups in thiabenzene 1-oxides examined are less polarized than those of the non-cyclic ylide compounds. In the case of XV, a hydrogen bond between the ester carbonyl and hydroxyl groups may be responsible for the low-frequency shift of the carbonyl absorption band.

The signals of the H-2 and H-6 protons in the n.m.r. spectra of these compounds appeared at a relatively high magnetic field, suggesting that there is no significant diamagnetic ring current, in accordance with the conclusion reached by Hortmann<sup>1</sup> and Cram.<sup>3</sup> The low field shifts of the H-5 proton signals may be a result of the combined anisotropic, mesomeric, and inductive effects of the carbonyl group (plus the inductive effect of the nitrogen atom in the case of XI).<sup>13</sup>

Preliminary study of the chemical properties revealed that VI is remarkably

stable. For example, it did not react with benzoyl chloride or acetyl chloride under refluxing conditions to recover unchanged.

Footnotes and References

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- 8 After melting at 155-160°, solidified and remelted at 170-174°.
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- 12 Unpublished work in this laboratory.
- 13 Further discussion of these spectral data will be given in a full paper.