

[J. Chem. Soc., Chem. Commun., 1987, 385]

**Novel Addition Products of 2-Aza-1-thiabenzene Derivatives with Methyl Propiolate.**

MIKIO HORI\*, TADASHI KATAOKA, HIROSHI SHIMIZU, KAZUNORI MATSUO, ATSUSHI SUGIMOTO, KOJI IKEDO, KOJI HAMADA, HARUO OGURA, and HIROAKI TAKAYANAGI

The addition reactions between 2-methyl-1-aza-2-thianaphthalene or 9-alkyl-10-aza-9-thiaphenanthrenes with methyl propiolate afforded novel 1:2-adducts, respectively, whose structures have been confirmed by an X-ray crystal structure determination. The X-ray structure shows no planarity of the 10-membered ring in spite of the  $10\pi$ -electron ring structure, showing lack of aromaticity. Further the possibility of a  $\sigma$ -sulphurane structure (trigonal bipyramidal) is slight, on the basis of the bond angles around sulphur, although the N--S distance (2.538 Å) is considerably shorter than the sum of the van der Waals radii of N and S (3.35 Å).

[Heterocycles, 26, 2365 (1987)]

**First Stable Selenabenzene Analogue, 2-Cyano-1-methyl-4-phenyl-1-selenanaphthalene : Synthesis and Reactions.**

MIKIO HORI\*, TADASHI KATAOKA, HIROSHI SHIMIZU, KAZUHIRO TSUTSUMI, SHINYA IMAOKA

2-Cyano-1-methyl-4-phenyl-1-selenanaphthalene was synthesized as the first isolable selenabenzene. Its ylidic structure was characterized by the spectral and chemical evidence. The thermal reaction of the selenanaphthalene afforded 1,2- and 1,4-rearranged products together with dimeric compounds. The photochemical reaction afforded the different 1,4-rearranged product, ketenimine and the photo-oxygenated product, 4-phenylcoumarin.

[Nippon Kagaku Kaishi (Special Articles on Organic Chemistry of Heteroatoms), 1987, 1323]

**Synthesis and Thermal Reactions of New Cyclic Sulfur Ylides possessing  $10\pi$  Electrons, 8-Alkyl-1,3-diphenyl-2H-dibenzo [b,f] cyclopenta [d] thiepinio-2-ides.**

MIKIO HORI\*, MITSUHITO OKITSU, TADASHI KATAOKA, HIROSHI SHIMIZU

A new cyclic sulfur ylide, 8-methyl-1,3-diphenyldibenzo [b,f] cyclopenta [d] thiepinio-2-ide was synthesized by deprotonation of the thiazulenium salt with sodium hydride. Other 8-alkyl derivatives were generated *in situ* and subjected to thermal reactions. The 8-methyl ylide underwent 1,4-rearrangement to give 3a-methyl-1,3-diphenyl-3aH-dibenzo [b,f] cyclopenta [d] thiepin (64%) together with the demethylated product (12%), whereas S-ethyl and S-propyl derivatives afforded the 1,4-rearranged products and the 1,2-rearranged products. This 1,2-rearrangement is unique and interesting because it proceeds at a cost of the benzenoid stabilization of a condensed benzene ring.