

[Tetrahedron Lett., 31, 7021 (1990)]

**Thermal Rearrangement of 9-Benzyl-10-aza-9-thiaphenanthrenes.**

HIROSHI SHIMIZU, KOJI IKEDO, KOJI HAMADA, HARUTOSHI MATSUMOTO,  
MICHINORI OZAWA, TADASHI KATAOKA, MIKIO HORI\*

Several 9-benzyl-10-aza-9-thiaphenanthrenium perchlorates (2) were prepared from the reaction of 2-amino-2'-benzylthiobiphenyls (1) with *N*-chlorosuccinimide or *t*-butylhypochlorite in dichloromethane at -78--50°C, followed by treatment with silver perchlorate. 9-Benzyl-10-aza-9-thiaphenanthrenes (3) generated from the azathiaphenanthrenium salts (2) by treatment with base such as *n*-BuLi in THF or aq. NaOH solution in dichloromethane underwent thermal 1,2-benzyl migration to give the corresponding 6-benzyl-6*H*-dibenzo(c,e)(1,2)thiazines (4) in moderate to good yields.

[Heterocycles, 30, 295 (1990)]

**Novel Reaction of a Stable Selenanaphthalene, 1-Cyano-2-methyl-2-selenanaphthalene with Electrophiles.**

MIKIO HORI\*, TADASHI KATAOKA, HIROSHI SHIMIZU, KAZUHIRO TSUTSUMI,  
MITSUHIRO YOSHIMATSU

Reactions of 1-cyano-2-methyl-2-selenanaphthalene (1) with dimethyl acetylenedicarboxylate gave benzocycloheptene derivatives and naphthalenedicarboxylate, while olefinic electrophiles such as acrylonitrile, methyl acrylate, and methyl vinyl ketone reacted with 1 to afford the cyclopropane derivatives.

[Heterocycles, 31, 23 (1990)]

**Synthesis of 1,2,3,4,5,6-Hexahydro-8-hydroxy-2,6-epithio-3-benzazocine.**

MIKIO HORI\*, HIROYUKI OZEKI, TATSUNORI IWAMURA, HIROSHI SHIMIZU,  
TADASHI KATAOKA, NORIYUKI IWATA

In anticipation of diminishing narcotism of 1,2,3,4,5,6-hexahydro-8-hydroxy-2,6-methano-3-benzazocine opioids, the corresponding 2,6-epithio-3-benzazocines have been synthesized by intramolecular cyclization of 1-(2-aminoethyl)-3,4-dihydro-1*H*-2-benzothiopyrans with *tert*-butylhypochlorite, and subsequent treatment of the 5-membered cyclic aminosulfonium salts with NaOH.