〔J. Chem. Soc., Chem. Commun., **1985**, 883〕

Novel Addition Reactions of New Cyclic Sulphur Ylides, 9-Alkyl-10-cyano-9-thiaphenanthrenes with Acetylenic Electrophiles. MIKIO HORI* TADASHI KATAOKA, HIROSHI SHIMIZU, OSAMU KOMATSU

The addition reactions of 10-cyano-9-methyl-9-thiaphenanthrene with dimethyl or diethyl acetylenedicarboxylate afforded the novel five-membered spiro product as 1:1-adduct via Sommlet-Hauser type rearrangement in 31.3% or 23.4% yield, respectively. On the contrary, the reaction of 10-cyano-9-ethyl-9-thiaphenanthene with acetylenic electrophile under similar reaction conditions gave a seven-membered dibenzothiepine derivative. On heating at 200°C in a sealed tube, the above spiro compounds underwent a thermal 1,5-rearrangement to give the corresponding nine-membered sulphur-containing heterocyclic compounds in high yields.

〔Tetrahedron Lett., **26**, 1321, (1985)〕

Thermolysis of 〔1, 2, 4〕Triazolo〔1, 5-a〕pyrimidine N-Ylides. MIKIO HORI*, KIYOMI TANAKA, TADASHI KATAOKA, HIROSHI SHIMIZU, EIJI IMAI, KAZUHIKO KIMURA, YOSHINOBU HASHIMOTO

5,7-Dimethyl〔1,2,4〕triazolo〔1,5-a〕pyrimidino-3-phenacylide generated by the reaction of an iminium salt (1) with 1 eq. of triethylamine, underwent a new thermal ring cleavage of the triazole moiety to give the pyrimidine derivative. However reaction of 1 with 2 eq. of triethylamine afforded the 2-iminooxazoline derivative. The iminooxazoline reacted with nucleophiles such as alcohols or amines to give imidazoles.

〔Heterocycles, **23**, 1381, (1985)〕

Formation of Novel Heterocycles, 〔1〕Benzothiopyrano〔3, 4-b〕pyrrole Derivatives by Unusual Cyclization Reaction of 1-Benzothiopyran 1-Oxide Derivatives MIKIO HORI*, TADASHI KATAOKA, HIROSHI SHIMIZU, EIJI IMAI, NORIYUKI IWATA, NORIHIRO KAWAMURA, MASAYASU KURONO

Treatment of 3-(2-ethoxycarbonylamino)ethyl-3-methyl-5-methoxy-2H-3,4-dihydro〔1〕benzothiopyran 1-oxide with sulfuryl chloride and then with sodium hydride afforded a novel type of derivatives of 〔1〕benzothiopyrano〔3,4-b〕pyrrole 1-oxide in 52% yield. The structure of product was confirmed by alternative synthesis from the reaction of 3H-3-(2-ethoxycarbonylamino)ethyl-3-methyl-5-methoxybenzothiopyran 1-oxide with NaH in 80% yield.