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Novel Addition Reactions of New Cyclic Sulphur Ylides, 9-Alkyl-10-cyano-9-thiaphenanthrenes with Acetylenic Electrophiles. MIKIO HORI*

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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 Sommet-Hauser type rearrangement in 31.3% or 23.4% yield, respectively. On the contrary, the reaction of 10-cyano-9-ethyl-9-thiaphenanthrene 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.

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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-iminoxazoline derivative. The iminoxazoline 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, EJI 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 sulfonyl 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.