〔Chem. Pharm. Bull., **36**, 3816 (1988)〕

Synthesis and Reactions of 1-Thianaphthalenes.

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Treatment of 1-methyl-4-phenyl-1-thio-2*H*-chromenium perchlorate with sodium hydride yielded a dimeric compound and two methyl-migrated compounds *via* unstable 1-methyl-4-phenyl-1-thianaphthalene. On the other hand, deprotonation of 2-cyano-1-methyl-4-phenyl-1-thio-2*H*-chromenium perchlorate with triethylamine in ethanol afforded 2-cyano-1-methyl-4-phenyl-1-thianaphthalene as stable yellow prisms. This is the first example of a stable and crystalline 1-thianaphthalene. Reaction of the stable 1-thianaphthalene with dimethyl acetylenedicarboxylate yielded a novel ring expansion product having nine-membered ring.

〔J. Chem. Soc., Perkin Trans. 1, **1988**, 1209〕

Syntheses and Reactions of 9-Substituted 10-Phenylthioxanthenium Salts: Negative Evidence for Thia-anthracene Oligomerisation.

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Various 9-aryl-10-phenylthioxanthenium salts have been prepared and their stereochemistry determined by ^{1}H n.m.r. spectroscopy. Reactions of the 10-phenylthioxanthenium salts or 10-phenyl-10-thia-anthracenes with aryl-lithiums have been studied in order to investigate whether or not 10-thia-anthracenes cause oligomerisation. The results indicate that the 10-phenyl-10-thia-anthracenes or the σ-sulphuranes of thioxanthenes do not cause oligomerisation.

〔J. Chem. Soc., Perkin Trans. 1, **1988**, 1885〕

Stable 2-Thianaphthalenes: Synthesis and Reactions with Electrophiles.

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The stable and crystalline 2-thianaphthalene derivatives, 2-methyl-2-thianaphthalene-1-carbonitrile (**1**) and 1-benzoyl-2-methyl-2-thianaphthalene (**2**) have been synthesized in high yields by proton abstraction from the corresponding benzothiopyrylium salts with triethylamine in ethanol. The ylidic nature of the 2-thianaphthalenes was established on the basis of spectral and chemical evidence. The reaction of **1** with dimethyl acetylenedicarboxylate (DMAD) in benzene afforded dihydrocyclopropa〔*a*〕naphthalene derivative and 5*H*-benzocycloheptene derivative. The reaction of **2** with DMAD afforded only a dihydrocyclopropa〔*a*〕naphthalene derivative, whose structure was determined by X-ray crystallography. Parallel reactions with other electrophiles gave a number of unexpected products.