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**10-Thia-anthracenes. Part 3. A Re-examination of the Reaction of 9-Phenylthioxanthylum Salt and Phenyl-lithium.**

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Reaction of 9-phenylthioxanthylum salt with phenyl-lithium afforded eight compounds, 9-phenyl-, 9,9-diphenyl-, 3,9-diphenyl-, 3,9,9-triphenyl-, and 4,9,9-triphenylthioxanthene, 9,9'-diphenyl-9,9'-bithioxanthenyl, thioxanthone, and 9,9'-diphenyldithioxanth-9-yl peroxide. Their structures were determined by comparison with the authentic samples. A radical mechanism contributed to the reaction of 9-phenylthioxanthylum salt with phenyl-lithium.

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**Reactions of Xanthinium *N*(7)-Ylides with Olefinic Dipolarophiles.**

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The stereo- and regio-chemical aspects of the reactions of xanthinium *N*(7)-methylides with olefinic dipolarophiles were elucidated. The reactions of ylides with *N*-phenylmaleimide afforded stereoselective *endo* adducts, and with acrylates and acrylonitrile afforded stereo- and regioselective 6-*endo* adducts. On the other hand, the reactions of ylides with *trans*-olefins afforded mixtures of two stereoisomers, the 8-*endo*-7-*exo* and 8-*exo*-7-*endo* pyrrolo(2,1-*f*)purine derivatives. Stereochemistry of the adducts was elucidated by <sup>1</sup>H n.m.r. and X-ray analysis. The stereoselectivity of the adducts was governed by the balance of steric and electronic effects. The ylides reacted in *Z*-form in all reactions investigated.

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**An Unexpected Double Cycloaddition of [1,2,4]Triazolo[1,5-*a*]pyrimidine *N*-Ylide with Activated Acetylenes and Alkenes.**

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The reaction of 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidino-3-phenacylide with activated acetylenes gave 1:2 adducts of ylide-R-C≡C-R. The structures of the products were determined as 3,3a-dihydropyrazolo[1,5-*c*]pyrimidine derivatives by hydrolysis, <sup>1</sup>H and <sup>13</sup>C n.m.r., and X-ray crystallography. Molecular orbital calculations (*ab initio*) of the model compounds were performed in order to elucidate the mechanism for the formation of the 1:2 adducts. The results of the calculations suggested that an intermediate, 1:1 adduct would be less reactive than the starting ylide. Easy formation of the 1:2 adducts can be explained by an equilibrium between the 1:1 adducts and the starting materials.