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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'-bithioxantheny1, 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.

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 1H 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.

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

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The reaction of 5,7-dimethyl[1,2,4]triazolo[1,5-α]pyrimidino-3-phenacyllyde with activated acetylenes gave 1:2 adducts of ylide-R=C=CR. The structures of the products were determined as 3,3a-dihydropyrazolo[1,5-c]pyrimidine derivatives by hydrolysis, 1H and 13C 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.