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CYCLOADDITION OF BENZOTHIAZOLIUM N-PHENACYLIDE WITH OLEFINIC DIPOLAROPHILES

Hiroshi Shimoharada, Michihiko Noguchi, and Otohiko Tsuge
Research Institute of Industrial Science, Kyushu University
Hakozaki, Higashi-ku, Fukuoka, Japan

Benzothiazolium N-phenacylide, generated in situ from 3-phenacylbenzothiazolium bromide and triethylamine, reacted with maleic anhydride, N-(p-methoxyphenyl)maleimide, dimethyl maleate, and fumarate to give the corresponding 1:1 adducts, tetrahydropyrrolo[2,1-b]benzothiazole derivatives, all of which were stable on treatment with triethylamine, in good yields respectively. In the reaction with maleonitrile the sole cycloadduct was formed in good yield, whereas fumaronitrile gave a mixture of two stereoisomeric cycloadducts whose relative yields were dependent on the reaction conditions. In some cases, dimer and/or hydrated compound of ylide were formed as by-products. On treatment with triethylamine epimerization and ring-transformation of cycloadducts obtained from both the dinitriles were observed. Stereochemistry of all cycloadducts was accomplished on the basis of spectral data.

Next, the reaction of N-phenacylide with triafulvenes was investigated. N-Phenacylide reacted with 4-cyano-1,2,4-triphenyl- and 4-cyano-4-ethoxycarbonyl-1,2-diphenyltriafulvene to give the corresponding [2 + 3] cycloadducts respectively. In the reaction with 4,4-dicyano-1,2-diphenyltriafulvene, however, cyclobutane derivative was formed with the elimination of benzothiazole.