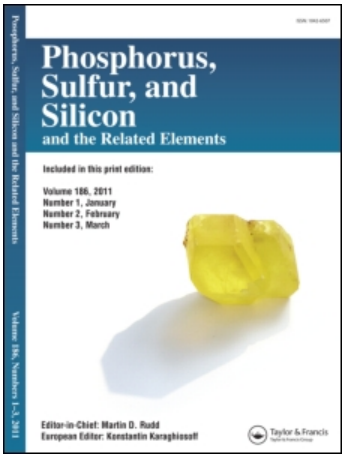

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Reactions of Thiazolo[3,2-*b*]-1,2,4-triazolium *N*-Ylides with Electron-deficient Acetylenes: Novel Benzoyl Migration of Intermediary 1:1-Adducts and Michael Addition to the Acetylenes

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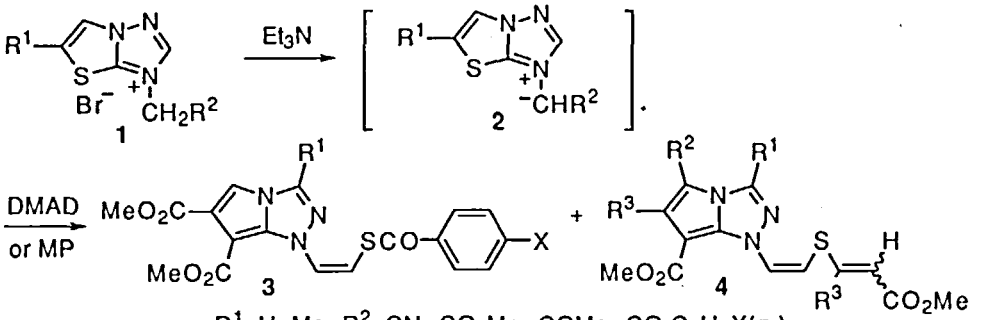
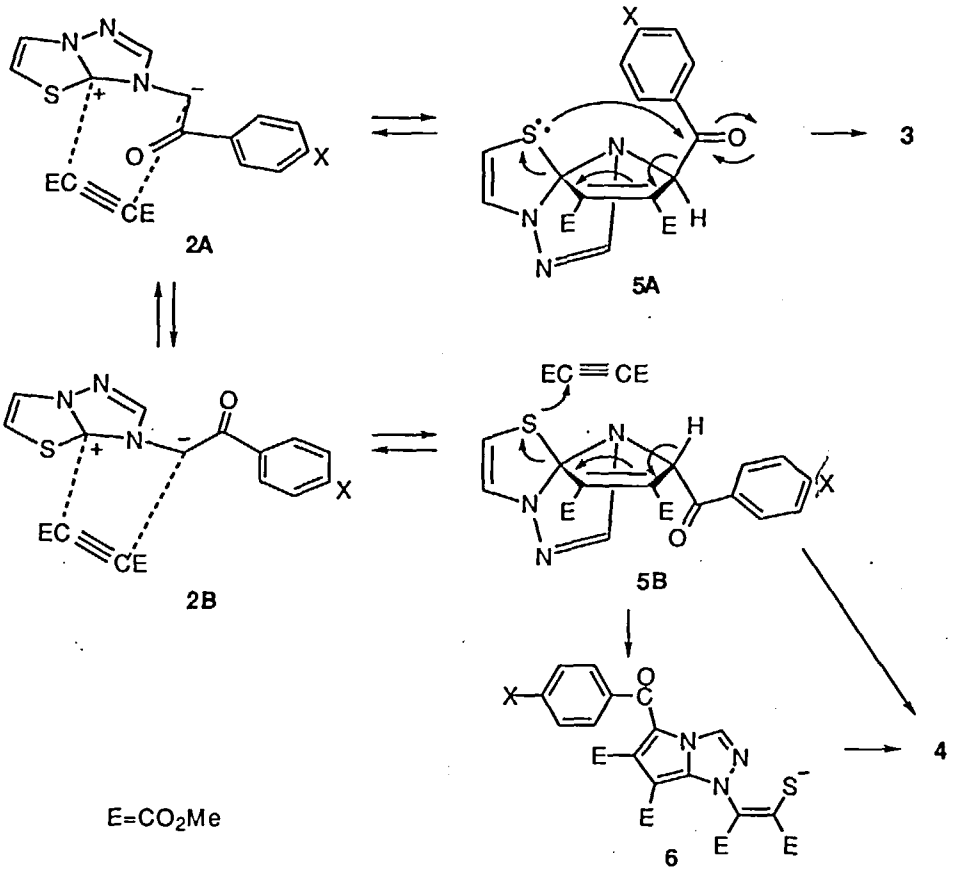
Abstract Reactions of thiazolo[3,2-*b*]-1,2,4-triazolium *N*-methylides with electron-deficient acetylenes gave the thiazole ring-opened products as a mixture of the *E*- and *Z*-isomers. In contrast, the *N*-phenacylides reacted with dimethyl acetylenedicarboxylate to give the thiobenzoates together with the thiazole ring-opened products. The mechanism for formation of these compounds is described.

The 1,3-dipolar cycloadditions are very useful reactions to construct new heterocycles. The triazolium *N*-methylides condensed by a pyridine[1] or a pyrimidine[2] reacted with dimethyl acetylenedicarboxylate (DMAD) to give the double 1,3-dipolar cycloaddition products. On the other hand, reactions of thiazolium and benzothiazolium *N*-phenacylides with DMAD gave the thiazole ring-opened products, in which two molecules of DMAD had been incorporated, and the hemithioacetals.[3]

We envisioned that novel reactivities could be achieved with thiazolo[3,2-*b*]-1,2,4-triazolium ylides, whose structure is the fused system of a triazole ring and a thiazole ring. The thiazolotriazolium *N*-ylides **2** were generated *in situ* from the thiazolotriazolium salts **1** and triethylamine, and allowed to react with equimolar amount of DMAD. The *N*-phenacylides provided the thiobenzoates **3** and the thiazole ring-opened products **4**.[4] The structures of these products were determined by spectral data



and X-ray crystallographic data. The formation mechanism for the thiol esters **3** is proposed on the basis of the crossover experiment and the reaction of the α-deuterated phenacyl derivative. The thiobenzoates **3** would be formed *via* the intramolecular benzoyl migration of the intermediary 1:1-adducts.



The reactions of other *N*-methylides **2** with 2 equiv. of methyl propiolate (MP) or DMAD afforded the thiazole-ring-opened products **4**. The reactions of **2** with MP at room temperature gave better yields than those at 0°C, whereas higher yields were obtained at 0°C in the reactions with DMAD.

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