CYCLOADDITION REACTIONS OF 1,3-DIPHENYLTHIENO[3.4-c]-1,2,5-OXADIAZOLE AND THERMAL BEHAVIOUR OF CYCLOADDUCTS

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1,3-Diphenylthieno[3.4-c]-1,2,5-oxadiazole (1), a nonclassical condensed 10π-electron heterocycle possessing tetravalent sulfur, undergoes 1,3-dipolar cycloaddition to maleimides to give a mixture of the corresponding exo-adducts 3 and endo-adducts 4. We have found that thermolysis of both the strained oxadiazoles of thianorbornane series 3 and 4 under mild conditions resulted in ring cleavage of the oxadiazole ring to nitrile and nitrile oxide moieties. That is, 3 and 4 reacted with olefins and acetylenes in boiling xylene or benzene to give the corresponding stereoisomeric cyano-isoxazolinylperhydrothieno[3.4-c]pyrrolediones and cyano-isoxazolylperhydrothieno-[3.4-c]pyrrolediones respectively.

In the reaction with acetylenes, 1 afforded a mixture of benzo[c]-1,2,5-oxadiazoles and 1:2 adducts. The former is the desulfurized compound of 1:1 cycloadduct and the latter is 1,3-cycloadduct of acetylene to nitrile oxide moiety generated from ring cleavage of the initial 1:1 cycloadduct.

In this context, thermal interconversion between stereoisomeric adducts of 1,3-diphenylthieno-[3.4-c]-1,2,5-thiadiazole to N-phenylmaleimide will be reported.