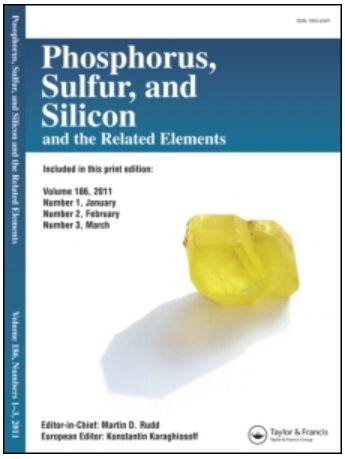

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SULPHUR CONTAINING HETERODIPOLAROPHILES. VARIABLE STEREOCHEMISTRY OF THE CYCLOADDITION OF THIOBENZOPHENONES TO KETENIMINES

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SULPHUR CONTAINING HETERODIPOLAROPHILES. VARIABLE STEREOCHEMISTRY OF THE CYCLOADDITION OF THIOBENZOPHENONES TO KETENIMINES

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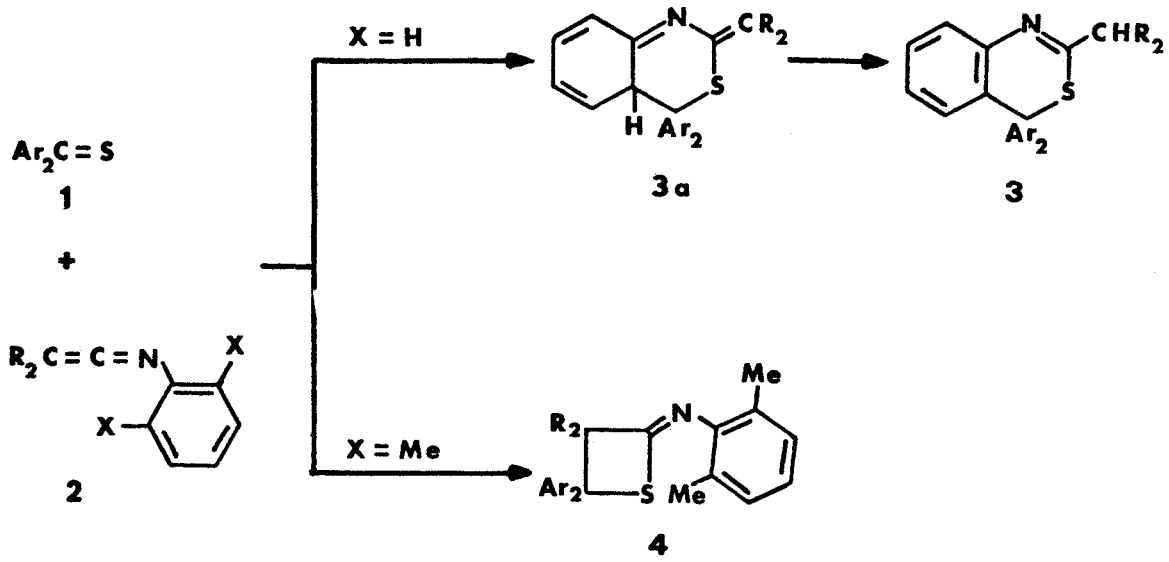
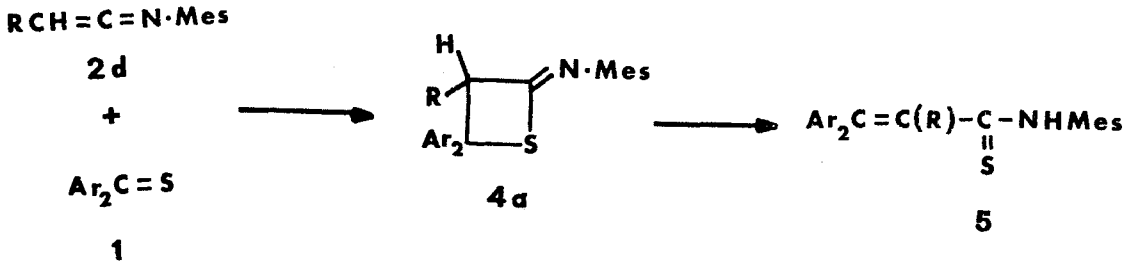
The thermal cycloaddition between thiobenzophenones (1) and ketenimines (2) takes place according to two reaction modes, the stereochemical course being determined by the type of substituent at nitrogen on the cumulene. Specifically, N-arylketenimines (2a) (X = H) react with (1) as a formal 4π system giving as final products 4H-3,1-benzothiazines (3) (1,4-cyclisation), whereas N-aryl ortho-disubstituted compounds (2b) (X = Me), as well as N-alkyl derivatives (2c), behave as 2π component to give 2-iminothietans (4) (1,2-cyclisation) (Scheme I). In the formation of the six membered ring compound (3), the ketenimine (2a) can be viewed to act as a 1,4-heterodiene to give the intermediate (3a) by addition of (1) across the C=N bond and the C=C of the N-aryl ring. Both reactions proved to be stereoselective.

Scheme I



The 1:1 adducts (3) and (4) were thermally stable under the reaction conditions, only the iminothietan derivatives (4a) deriving from the partially substituted ketenimines (2d) rearrange to thioamides (5) (Scheme II).

Scheme II



Experimental (kinetic, PES, search for intermediates) and theoretical (orbital analysis, ab initio computation) approaches have been equally employed in order to choose, among various mechanistic possibilities, the reaction pathways leading to (3) and (4).