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LIGHT-INDUCED FORMATION OF STABLE THIETES

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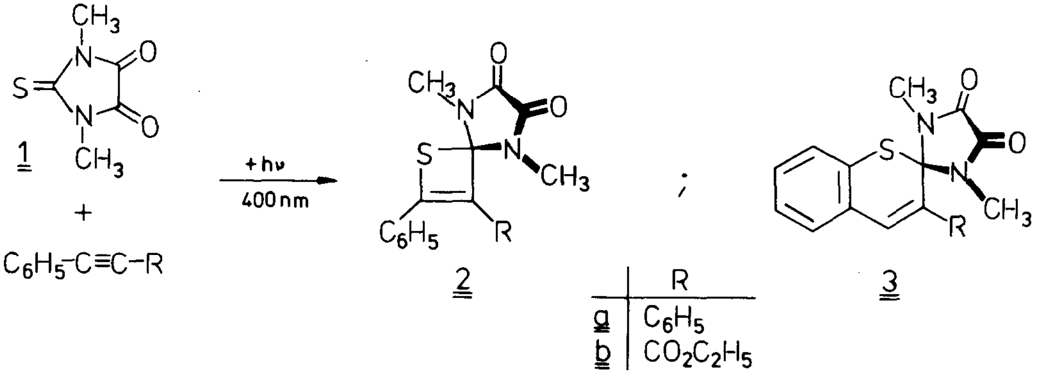
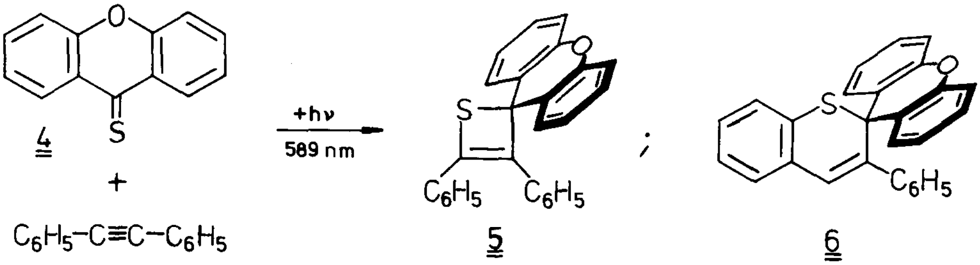
In a previous communication we had reported that the light-induced reactions of 1,3-dimethyl 2-thioparabanate (1) or xanthione (4) with phenylacetylene derivatives gave 1:1 adducts 3a,b or 6, respectively[1]. Previously assigned structures of these adducts were based mainly on spectroscopic data and analytical results. An X-ray crystal structure analysis of the adduct thought to have structure 3a, has now shown that this adduct has in fact the thiete structure 2a.



	R
a	C_6H_5
b	$CO_2C_2H_5$



2a crystallizes from methanol in the orthorhombic space group D_{2h}^{15}-Pbca with a=14.164, b=12.766, c=18.736 Å and eight molecules per unit cell. On a CAD-4 diffractometer, 3505 independent reflections were measured with Ni-filtered Cu $K_{\bar{\alpha}}$-radiation. The molecular structure of 2a, the nonhydrogen atoms of which are shown in the FIGURE 1, converged with R=0.047 and R_w=0.051 (2131 observed reflections).

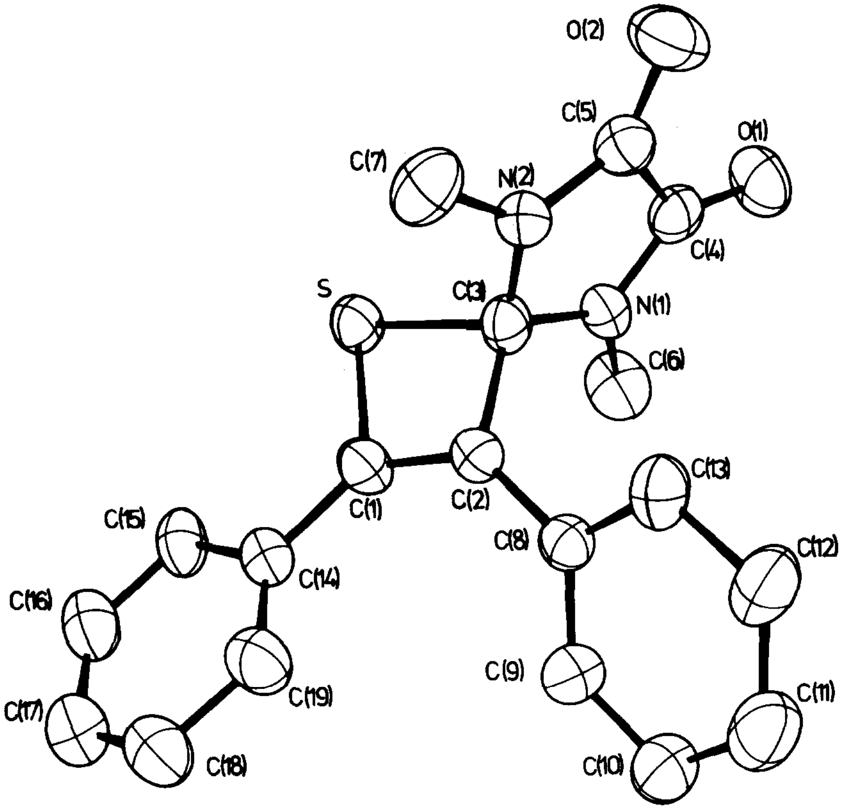


FIGURE 1. Molecular structure of 2a

From this result we conclude that the analogous photoadduct derived from 1 and ethyl phenylpropiolate has structure 2b instead of 3b. Accordingly structure 6 of the adduct from 4 and diphenylacetylene should be replaced by formula 5.

To our knowledge, this is the first case where stable thiete derivatives are generated photochemically. Thietes have been previously postulated as unstable intermediates[1,2] in photochemical reaction pathways, and their thermal formation has been described in few cases[3].

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