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PHOTOCHEMICAL AND THERMAL (2+2) ADDITION OF THIONES TO HETERO-SUBSTITUTED ACETYLENES. REARRANGEMENT OF INTERMEDIATE THIETES TO α,β-UNSATURATED DITHIOESTERS AND THIOAMIDES

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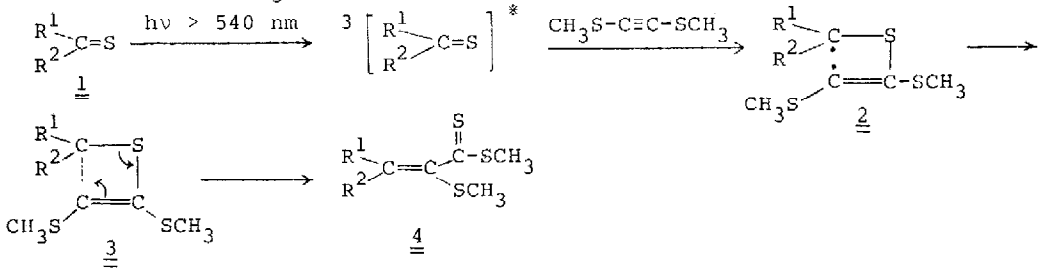
Irradiation of a benzene solution of 9-xanthenethione (1: R^1,R^2= C_6H_4-O-C_6H_4 and bis(methylthio)ethyne afforded the α,β-unsaturated dithioester 4: R^1,R^2= C_6H_4-O-C_6H_4); after chromatography (silica, benzene-pentane 1:3) orange coloured crystals (m.p. 149.5 - 150°) were isolated in 70% yield. Its structure wa deduced from IR, MS, UV and NMR spectra. UV (CCl_4): maxima (nm) at ≈520 (ε ≈1.6 × 10^2,sh), 428 (ε= 1.65 × 10^3), 332 (ε= 8.3 × 10^3), 278 (ε= 5.8 × 10^3); ^{1}H-NMR ($CDCl_3$, δ^{TMS}= 0): δ= 2.15(s), δ= 2.62(s), δ= 6.78 - 8.10(m); ^{13}C-NMR($CDCl_3$, δ^{TMS}= 0); δ= 229.8 (C=S), δ= 136.2(=C^{β}), δ= 125.8(=C^{α}), δ= 20.2 (SCH_3, dithioester), δ= 16.2 (=C-SCH_3) (*cf.* [1]).

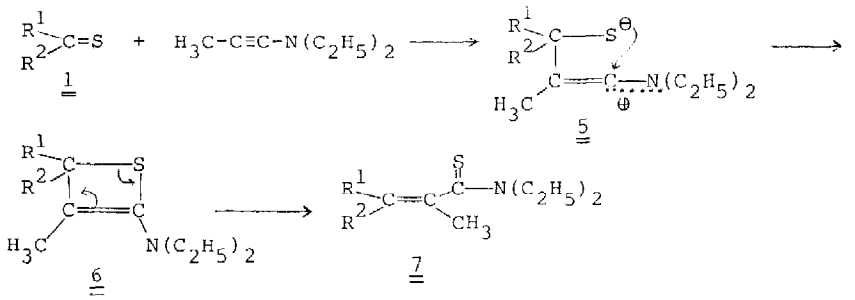


From 9-fluorenethione (1: R^1,R^2= C_6H_4-C_6H_4) and thiobenzophenone (1: R^1=R^2= Ph) similar dithioesters 4 were obtained (m.p. 110-111° and 142.5 - 143.5°) respectively) in 30% yields (silica, ether - pentane 1:40).

In the latter case some 3,3,5,5-tetraphenyl-1,2,4-trithiolane[2] and 3,4-bis(methylthio)-1-phenyl-1,2-dihydro-2-thianaphtalene (≈10% m.p. 81.5 - 83°) was formed (*cf.* [3]). When the irradiation was performed at -60°, this adduct could not be found; it was not formed at room temperature in the dark[4].

The formation of a dithioester 4 proceeds undoubtedly via a biradical 2 and an unstable thiete 3[5], which rearranges analogously to an oxete[6].

Thermal reaction of 9-xanthenethione (1: R^1,R^2= C_6H_4) and 1-diethylamino-1--propyne in benzene at room temperature (60 hrs) yielded the α,β-unsaturated thioamide (7: R^1,R^2= C_6H_4-O-C_6H_4), isolated by chromatography (silica, benzene-pentane) as slightly yellow coloured crystals (yield 75%, m.p. 85.2 - 86.5°).



Its structure was confirmed by MS, IR, UV and NMR spectra. UV (CCl_4): maxima (nm) at 375 ($\varepsilon = 9.4 \times 10^2$); 325 ($\varepsilon = 1.3 \times 10^4$), 304 ($\varepsilon = 1.4 \times 10^4$,sh), 282 ($\varepsilon = 1.9 \times 10^4$); *cf.*[7]; ^{1}H-NMR ($CDCl_3$, $\delta^{TMS} = 0$): $\delta = 0.72$(t), $\delta = 1.20$(t), $\delta = 2.26$(s), $\delta = 2.85 - 4.65$(m), $\delta = 6.80 - 8.20$(m), ^{13}C-NMR ($CDCl_3$, $\delta^{TMS} = 0$); $\delta = 201.2$ (C=S), $\delta = 133.3$ ($=C^{\beta}$), $\delta = 119.2$ ($=C^{\alpha}$), $\delta = 46.7$ and $\delta = 44.8$ ($N-CH_2-$), $\delta = 22.6$ ($\underline{C}H_3-C=C$), $\delta = 12.5$ and $\delta = 10.4$ ($N-CH_2-\underline{C}H_3$); *cf.*[1,8].

From thiobenzophenone an analogous thioamide (7: $R^1=R^2=Ph$) was obtained in 60% yield (m.p. 105 - 106.5°, silica, ether - pentane 1:20).

The thermal addition probably involves a dipolar intermediate 5 leading to an unstable thiete 6, which rearranges to 7.

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