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PHOTOCHEMICAL (2+2)-CYCLOADDITION OF THIOXANTHENETHIONE WITH SOME BUTATRIENE DERIVATIVES

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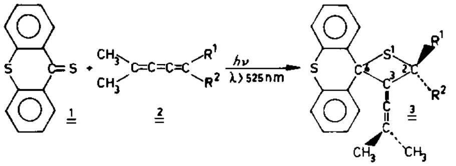
Abstract: Irradiation of thioxanthenethione 1 with the alkyl- and alkoxysubstituted butatrienes 2*a*-*d* gives the thietanes 3*a*-*d*. Using 2*d* the cyclobutanethione 6 is formed as a byproduct. Free radical addition of iC_3H_7SH to 2*a* predominantly occurs via terminal attack of the thiyl radical on the π-system.

As an extension of our studies on the photochemical (2+2)- and (4+2)-cycloadditions of thiocarbonyl compounds with acetylenes[1], allenes[2] and ketenimines[3] we have investigated the regiospecificity and the course of the reaction of an excited thione with some cumulated trienes. Thus irradiation of a 0.050 molar dichloromethane solution of xanthenethione 1 and 200 mol % of butatriene derivatives 2*a*-*d* through a $K_2Cr_2O_7$-filter solution (T<1‰ at λ>525 nm) furnished the 3-(2-methyl-1-propenyl-idene)thietanes 3*a*-*d*.



a:R^1=H R^2=OCH_3
b:R^1=H R^2=OtC_4H_9
c:R^1=H R^2=OPh
d:R^1=CH_3 R^2=CH_3

According to ^1H NMR analysis thietanes 3*a*-*c* were obtained in over 90% yield. Isomeric adducts were not detected. Compound 3*d* was formed in a yield of about 70% and was contaminated with 15% of an isomeric byproduct (*vide infra*). The thietanes 3*b* and 3*c* were obtained pure by crystallization from CH_2Cl_2-CH_3OH, while thietanes 3*a* and 3*d* were purified by chromatography (SiO_2/benzene-pentane-ether).

The structure of the thietanes 3*a*-*d* followed from their ^{13}C NMR-, ^1H NMR-, mass- and UV-spectra. For 3*b* for instance the following spectroscopic data were found:

^{13}C NMR($CDCl_3$):δ20.1 and 20.4($2xCH_3$),δ27.8 and 75.7(tC_4H_9),δ58.8(C^4),δ74.8(C^2),δ102.9($(CH_3)_2\underline{C}$=), δ104.2(-C^3=),δ123.7-140.6(12 aromatic C),δ198.6(=C=).

^1H NMR($CDCl_3$):δ1.18(s,tC_4H_9),δ1.91(s,CH_3),δ1.99(s,CH_3),δ6.07(s,-CHO-),δ7.0-7.5(m,6 aromatic H), δ7.8-8.0(m, 2 aromatic H).

UV(hexane),λ_{max}/nm($\varepsilon/m^2.mol^{-1}$):297(308,sh),266(1306).

MS showed amongst others peaks corresponding to $[M^{+\cdot} - Ar_2C{=}S]$, $[M^{+\cdot} - (CH_3)_2C{=}C{=}C{=}CHO\textit{t}C_4H_9]$, $[M^{+\cdot} - Ar_2C{=}C{=}C{=}C(CH_3)_2{+}H]$, $[M^{+\cdot} - S{=}CHO\textit{t}C_4H_9{-}H]$.

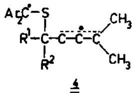
Apparently, triplet thioxanthenethione preferably attacks the end of the triene system with formation of the stable biradical 4 from which 3 is formed upon ringclosure.

The isomeric byproduct found starting from 2*d* was the cyclobutanethione derivative 6, which structure was deduced from the following NMR data:

^{13}C NMR(CDCl$_3$):δ22.3 and 25.0(=C($\underline{C}$H$_3$)$_2$),δ24.8(C^2($\underline{C}$H$_3$)$_2$),δ61.7(C^3,spiro),δ69.1(C^2),δ125.4-151.3 (12 aromatic C + 2 vinylic C),δ252.3(C=S).

^{1}H NMR(CDCl$_3$):δ0.74(s,2xCH$_3$),δ1.59(s,CH$_3$),δ2.56(s,CH$_3$),δ7.00-7.60(8 aromatic H).

The formation of this thione can be rationalized by assuming attack of excited 1 on C^2 of the π-system, ringclosure of the biradical thus formed into the thietane 5 and subsequent rearrangement of 5 into 6; *cf.* ref. 3.



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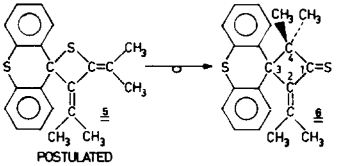
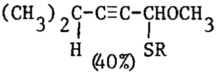
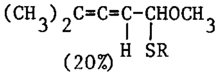
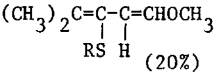
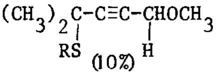


In the literature the regiospecificity of reactions with excited thiones generally parallels that with RS radicals[4]. In order to study this for alkoxybutatrienes we treated 2*a* under free radical conditions with *i*C$_3$H$_7$SH and obtained four adducts in yields of 10-40%, which were separated by GLC and identified by spectroscopy:


$(CH_3)_2\underset{H}{C}{-}C{\equiv}C{-}\underset{SR}{C}HOCH_3$ (40%)


$(CH_3)_2C{=}C{=}\underset{H}{C}{-}\underset{SR}{C}HOCH_3$ (20%)


$(CH_3)_2C{=}\underset{RS}{C}{-}\underset{H}{C}{=}CHOCH_3$ (20%)


$(CH_3)_2\underset{RS}{C}{-}C{\equiv}C{-}\underset{H}{C}HOCH_3$ (10%)

This result shows that terminal attack of the thiyl radical on this triene system accounts for 70% of the products.

In the case of alkylsubstituted 1,3-butadienes only terminal attack of excited thiones and RS radicals on the π-system has been reported[5,6,7].

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