Tetrahedron Letters Vol. 22, pp 1139 - 1140
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0040-4039/81/0315-1139$02.00/0

PHOTOCHEMICAL AND THERMAL (2+2)-CYCLOADDITION OF THIOXANTHENETHIONE TO SOME ALIPHATIC PENTATETRAENES

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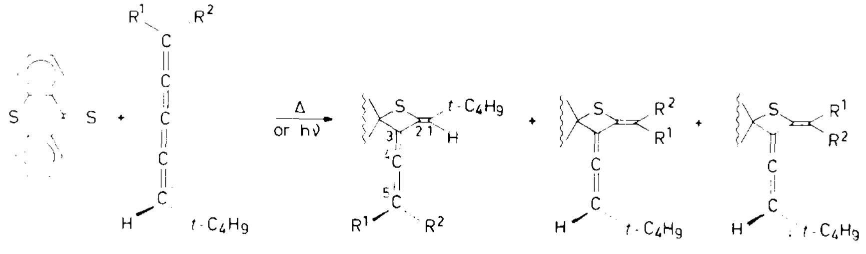
Abstract: Reaction of thioxanthene-9-thione 1 with the alkyl substituted pentatetraenes 2a-g gives mixtures of the thietanes 3a-g and 4a-g. The ratio 3/4 in the thermal reaction is strongly dependent on the substituents. In the case of 2a thermal rearrangement of the product leads to a stable thiete.

During the last decade we investigated the photochemical reactions of thiocarbonyl compounds with acetylenes[1], allenes[2], ketenimines[3] and butatrienes[4](cf.5). Now, we wish to report on the photochemical and thermal (2+2)-cycloadditions of an aromatic thione to pentatetraenes, compounds which have become readily available[6].

The thermal reaction is so fast that photochemical reactions had to be carried out in dilute solution at about -70°C.

Thus irradiation of a 0.005 molar dichloromethane solution of thioxanthenethione 1 and 100-150 mole% of pentatetraene 2 through a $K_2Cr_2O_7$-filter solution (T < 1% at λ < 525 nm) furnished generally mixtures of the thietanes 3Z, 4E and 4Z. Other isomeric adducts were not present (^{1}H NMR).



1 2a-g 3Z 4E 4Z

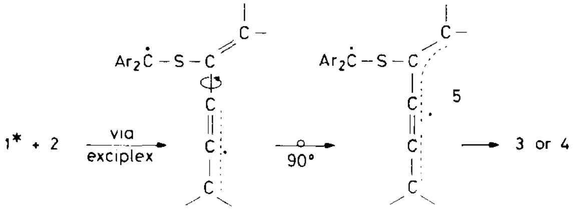
Thermal reaction of thioxanthenethione 1 and the pentatetraene 2 (about 0.02 molar solution of each in CH_2Cl_2) generally occurred within 15 minutes at roomtemperature with formation of the same adducts (see Table). Except for 3c and 4c the products were reasonable stable and could be purified by column chromatography[7]. Isolated yields were usually larger than 60%. The structures of the thietanes 3 and 4 followed from their ^{13}C NMR, ^{1}H NMR, IR, UV and mass spectra. For 3a (=4a) for instance the following spectroscopic data were found.

^{13}C NMR ($CDCl_3$): $\delta 109.5(C^3)$, $\delta 109.9(C^5)$, $\delta 136.9(C^1)$, $\delta 199.4(C^4)$; ^1H NMR: $\delta 5.32(d,1H,{}^6J_{1,5}=1.7Hz)$ $\delta 5.74(d,1H,{}^6J_{1,5}=1.7Hz)$, $\delta 7.0$-7.5(m,6 arom. H), $\delta 7.8$-7.95(m,1 arom. H), $\delta 8.13$-8.28(m,1 arom. H) IR(KBr): 1943 cm^{-1} and 1915 cm^{-1} (C=C=C), 1615 cm^{-1} (C=C); UV(hexane): λ_{max}/nm ($\varepsilon/m^2.mol^{-1}$): 300 (580), 265 (1160).

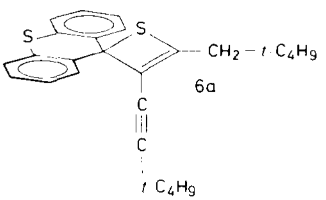
The chemical shifts of the protons of 3Z, 4E and 4Z were assigned by heteronuclear NOE on 3a. The vinylic protons of 3Z appear as sharp singlets around δ=5.3 ppm. The allenic protons of 4Z appear as sharp singlets around δ=5.8 ppm. The protons of 4E appear as broad multiplets around δ=5.9 ppm, possibly due to coupling through 7 bonds with the substituent R^1 or R^2.

	substituents	ratio thermal	photochemical	Δ and hν
		3:(4E+4Z)	3:(4E+4Z)	4E:4Z
a:	R^1=H,R^2=t-C_4H_9	(3=4)	(3=4)	<10:90
b:	R^1=H,R^2=i-C_3H_7	35:65	60:40	<10:90
c:	R^1=R^2=$(CH_2)_4$	55:45	45:55	(4E=4Z)
d:	R^1=R^2=CH_3	75:25	-	(4E=4Z)
e:	R^1=CH_3, R^2=C_2H_5	80:20	-	~50:50
f:	R^1=CH_3,R^2=i-C_3H_7	85:15	-	~50:50
g:	R^1=CH_3,R^2=t-C_4H_9	90:10	45:55	<10:90(hν)

We can rationalize the photochemical addition reaction by assuming attack of the triplet thione at both ends of the two 1,3-diene systems in the pentatetraenes with formation of an allylic biradical. The formation of biradical 5, probably via an exciplex, is in accordance with predominant formation of the most stable biradical by bond formation at C(2) and C(4) of the pentatetraene system.



5



6a

As we observe the same products and the same E/Z ratios (^1H NMR) by both photochemical and thermal reactions, we suppose the same intermediate biradicals. At roomtemperature the thietane 3a, dissolved in $CDCl_3$, slowly isomerises into the alkynylthiete 6a.

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7. Column chromatography was performed (hexane with 4% of dichloromethane) over phenylated silica,prepared according D.C. Locke, Anal. Chem., 44, 90 (1972), using Kieselgel 60 (230-400 mesh),$TiCl_4$ and PhMgBr in ether.

(Received in UK 2 January 1981)