THERMAL ADDITION OF XANTHENETHIONE TO ALLENES: "A CONCERTED TWO STEP"

 $(\pi^2 + \pi^2 + \pi^2) - CYCLOADDITION$

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Abstract: (2+2) - and (4+2)-cycloadducts are formed by thermal reaction of xanthenethione with allenes. Activation parameters for this "concerted two step" $(\pi^2 + \pi^2 + \pi^2)$ reaction are presented.

Photochemical addition of thiones to allenes have well been studied¹. However, thermal additions between thiones and allenes have not received attention this far. In this paper, evidence is presented that such thermal reactions are quite well possible. Thus xanthenethione 1 reacts with allenes $H_2C=C=C(X)R$ (2: X = NMe₂, OtBu, StBu or Ph; R = H or D) at 25°C in degassed solutions to give two (2+2)-cycloadducts (thietanes 3 and 4) and one (4+2)-cycloadduct (thiopyran 5) in a total yield of 80 - 95%. In the case of X = Ph also a small amount of the (4+2)-cycloadditionproduct 6 is formed.



The reaction shows, as expected second order kinetics (solvent CDCl_3 , measured by ¹H NMR). Electron donating substituents in the allenic system increase the reaction rate. The reaction of 1 with 2d is 100 times faster than with 2e. Rate constant k₂ (298K) = 5.89.10⁻⁵ dm³.mol⁻¹.s⁻¹ for 2e with ΔG^{\neq} = 97 kJ.mol⁻¹; ΔS^{\neq} = -203 J.mol⁻¹K⁻¹; ΔH^{\neq} = 36 kJ.mol⁻¹.

The polarity of the solvent influences the reaction rate; the following relative k_2 -values were found; 1.0 (C_6D_6 ; $\varepsilon = 2.28$), 1.4 ($CDCl_3$; $\varepsilon = 4.58$) and 3.0 ($1,2-C_6H_4Cl_2$; $\varepsilon = 9.93$). For the addition reactions of xanthenethione to (dimethylamino)allene the ratio k_2 (MeCN; $\varepsilon = 37.5$) / k_2 (hexane; $\varepsilon = 1.88$) was 8.0 (measured by UV-spectroscopy). These solvent effects are small however, and therefore exclude a mechanism *via* dipolar intermediates (*c.f* Huisgen²). A charge transfer complex as reaction intermediate is unlikely, because of the absence of the absorption band for such an intermediate in the region 400 - 2500 nm (studied for the reaction of 1 with phenylallene 2*e*). The investigated reactions show typical features of a one step process, viz little change in rate with changing polarity of the solvent, a relatively small activation energy, and a relatively large negative activation entropy³. However, in the case of a one step process one should not expect three or four adducts.

The photoaddition of 1 to allenes 2, which gives the same products 3, 4 and 5 albeit in a slightly different ratio, undoubtedly proceeds through a 1,4-biradical adduct¹. The comparable results for the thermal and the photochemical reaction, hint to a common intermediate. We therefore propose for the thermal reaction " an orbital concerted", but "energetically non-concerted" process, also been called "a concerted two step process" 4,5 .

In our case this implies the initial formation of the allylic biradical $\frac{8}{2}$ (see Scheme 1) by interaction of the π -bond of the thiocarbonyl group with both double bonds of the allene system and concomitant formation of the C-S bond and rotation around the C(1)-C(2) bond. This step is followed by disrotatory ring closure with formation of thietane $\frac{3}{2}$ or $\frac{4}{2}$.



The high ratio $\frac{4Z}{4E} > 95/5$ is conceivable from a preferential approach of the sulfur atom of the thione at the least hindered site of the conjugated double bond of the allene. The observation of an ESR-signal during the thermal reaction also points to the intermediary of a biradical adduct⁶. The photochemical addition of thiones to pentatetraenes gives a stable pentadienylic biradical *via* a non-pentadienylic intermediate. As was recently found, pentatetraenes R₂C=C=C=C=C

 R_2^1 also undergo thermal addition of thiones⁷, but olefins and butatrienes do not react thermally. This observation supports our mechanism, as pentatetraenes can be converted into a thermodynamically stable pentadienylic biradical adduct by addition of thione *via* the same $({}_{\pi}^2 {}_{s} + {}_{\pi}^2 {}_{s} + {}_{\pi}^2 {}_{s})$ -mechanism as discussed. Starting from olefins no allylic or pentadienlyic biradicals can be formed, while in the case of butatrienes $R_2^{C=C=C=CR_2^1}$ formation of an allylic biradical would be accompanied by loosing conjugation with a terminal double bond.

References

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