

PHOTOCYCLOADDITION REACTIONS OF THE FIRST STABLE THIOALDEHYDE:

2,4,6-TRI(*tert*-BUTYL)THIOBENZALDEHYDE WITH SUBSTITUTED ALLENES

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Abstract: Irradiation of 2,4,6-tri-(*tert*-butyl)thiobenzaldehyde **1** with some alkoxy-, alkylthio-, and phenyl-allenes **2a-i** gave one stereoisomer of a (2+2)-cycloadduct, *viz.* thietane **3** in high yields (75-95%). Ringclosure is in agreement with MNDO-calculations.

Recently, a number of investigations on photochemical¹⁻³ and thermal⁴ cycloaddition reactions of *aromatic thiones* with allenes and other cumulated systems have been carried out in our laboratory.

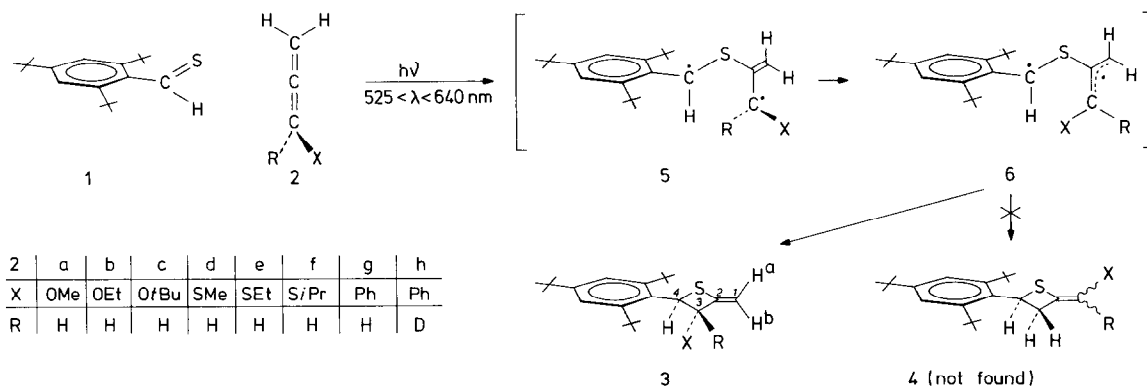
Until recently, it was too difficult to investigate the photochemical behaviour of monomeric thioaldehydes, because of their extreme instability. Simple thioaldehydes like thioformaldehyde and thiobenzaldehyde are so unstable that they can only be detected spectroscopically or by chemical trapping experiments⁵⁻⁸.

In 1982 R. Okazaki *et al.* published the synthesis of the first stable thioaldehyde e.g.: 2,4,6-tri-(*tert*-butyl)thiobenzaldehyde **1**⁹⁻¹⁰.

In the course of our studies on the photochemical (2+2)- and (4+2)-cycloaddition reactions of aromatic thiocarbonyl compounds with unsaturated cumulated systems, we were anxious to know the photochemical behaviour of thioaldehyde **1**. We therefore extended our investigations with a study of the regiospecificity of the addition of excited thioaldehyde **1** to substituted allenes.

Irradiation of a 0.030 molar deuteriochloroform solution of the pink thioaldehyde **1** and 0.5 molar allene (X = OMe, OEt, OtBu, SMe, SEt, SiPr, Ph, R = H or D), through a K₂Cr₂O₇/CuSO₄/H₂O filter solution (T = 1% at 525 and at 640 nm) gave after a few hours, a colourless reaction mixture. After evaporation of the solvent at 20°C *in vacuo* (0.01 mm/Hg) a pure adduct was obtained in high yield.

Reactionscheme



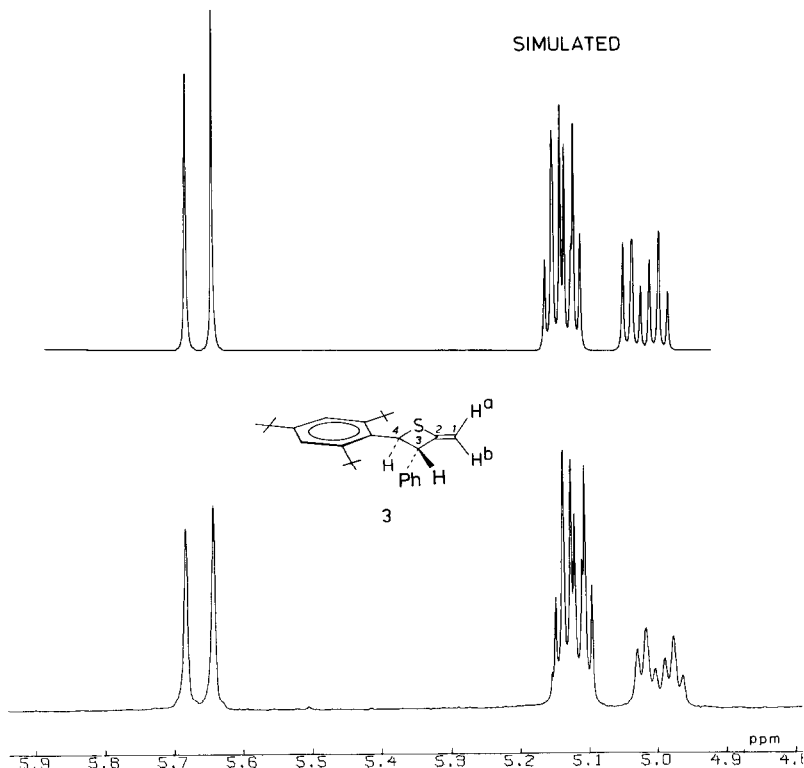
Mass spectroscopy showed that we are dealing with a 1:1 adduct. The spectroscopic data (^1H NMR, ^{13}C NMR, IR, UV) were compatible with the structure of (2+2)-cycloadduct thietane 3, but incompatible with the structure of thietane 4 (see Scheme). Spectroscopic data for thietane 3, X = OEt: ^1H NMR (CDCl_3) 90 MHz, first order); 5.26 (dd, H_a , $^2\text{J} = 2.1$ Hz, $^4\text{J} = 2.1$ Hz), δ 4.90 (dd, H_b , $^2\text{J} = 2.4$, $^4\text{J} = 2.1$ Hz), δ 4.86 (H^3 , d, t, $^3\text{J} = 7.2$ Hz, $^4\text{J} = 2.4$ Hz), δ 5.87 (H^4 , d, $^3\text{J} = 7.2$ Hz). ^{13}C NMR (CDCl_3); 103.6 (=C H_2), 145.8 (S-C 2 =), 90.0 (HC 3 -OR), 52.4 (H-C 4 -S) ppm. IR (oil); $\bar{\nu}$ (C=C) = 1640 cm^{-1} . UV (hexane); $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{m}^2 \text{mol}^{-1}$); 249.6 (837), 216 (1075) 336 (sh) 369 (sh). The spectroscopic data for the thietanes 3 (X = OMe, OtBu, SMe, SEt, SiPr, Ph) were generally very similar. Further structural proof for 3 was found by the reaction of thioaldehyde 1 with PhCD=C=CH $_2$ (2h).

The ^1H NMR pattern (200 MHz) for (2+2)-cycloadduct 3 (X = Ph, R-H) could be simulated very well (see Fig.) resulting in $^2\text{J} = 2.09$ Hz, $^3\text{J} = 8.00$ Hz, $^4\text{J} = 2.45$ Hz. The magnitude of the coupling constants, $^3\text{J} = 7.2$ -8.0 Hz, suggests a *trans* stereochemistry for the substituents at the thietane ring (c.f.¹¹). With alkoxy- and alkylthioallenes (2a-f) also only thietane 3 is formed and no trace of thietane 4 could be detected. This latter type of thietane (4) is always formed in cycloaddition reactions of *aromatic* thiones simultaneously with isomer 3.¹

Starting from alkoxyallenes a byproduct of very high molecular weight was formed, albeit in a very low yield (< 5%). Its exact structure was not elucidated.

Discussion

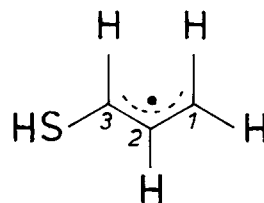
Because fast intersystem crossing from $\text{S}_1 \rightarrow \text{T}_1$ in the thioaldehyde is to be



expected, the reaction will occur from its T_1 state. Central attachment of the sulfur atom of the thiobenzaldehyde 1 is in accordance with preferential formation of the thermodynamically most stable biradical 1 (5, see Scheme). This 1,4-biradical will gain stabilization energy by (a very fast) rotation of 90° around a C-C bond, resulting in the allylic 1,4-biradical 6 (c.f. 1), which will give ring closure with formation of the sterically less hindered thietane 3.

The unexpected selectivity of the ring closure at C(3) in the intermediary 1,4-biradical 6 will be due to two important phenomena, *viz.* electronic structure and steric crowding. MNDO¹² calculations on the model system $H_2\bar{C}-\dot{C}H-\dot{C}(X)R$ with $X = O$ or S indicate that in the intermediary 1,4-biradical the electron density in the highest π -bonding orbital at C(3) is appreciably higher than at C(1) (see Table).

	C(1)	C(2)	C(3)	S
ψ^2	0.37	0.00	0.53	0.10
atomic charge	-0.065	-0.055	-0.175	0.045



Thus it is conceivable that ring closure on C(3) is preferable to that on C(1). The calculations therefore, are in agreement with the exclusive formation of thietane 3.

That diaryl thioketones with allenes also can produce isomer 4, is probably due to sterical crowding of the two arylgroups which hinders the formation of isomer 3. This assumption is supported by the fact that in the reaction of xanthenethione with allene 2, the yield of thietane 3 decreases with increasing size of R ($X = OR$ or SR).¹

In cycloaddition reactions of triplet carbonyl- and thiocarbonyl compounds to ethylenic compounds, energy loss (low quantum yields and cis/trans isomeri-

zation) are explained by disproportionation of the intermediary 1,4-biradicals into ground state starting compounds.

Irradiation of thioaldehyde 1 with a two-fold excess of optically active (+)-1,3-diphenylallene 2i (PhC(H)=C=C(H)Ph , $[\alpha_D] = +54$)¹³ showed no racemization of recovered 1,3-diphenylallene. Thus, there is no detectable disproportionation of the intermediary biradical 6; therefore, ring closure has to be much faster than disproportionation.

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10. To a 0.02 M solution of 2,4,6-tri-(*tert*-butyl)bromobenzene^{10b} in dry ether 0.02 M of a butyllithium solution (1.5 M in hexane) was added. The temperature was raised to reflux temperature and this was continued for one hour. At -80°C, 100 ml of dry tetrahydrofuran was added. To this solution a large excess (5 ml) of *O*-ethyl thioformate^{10c} was added. The temperature was allowed to rise to room temperature and the solution was stirred at RT for another 2 hours. Washing with water and extracting with hexane gave, after drying and evaporation, in 30-40% overall yield the pink solid 2,4,6-tri-(*tert*-butyl)thiobenzaldehyde. Further purification was accomplished by preparative HPLC. (Eluent hexane, column material Kieselgel 60, 30-200 mesh, Merck)
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