

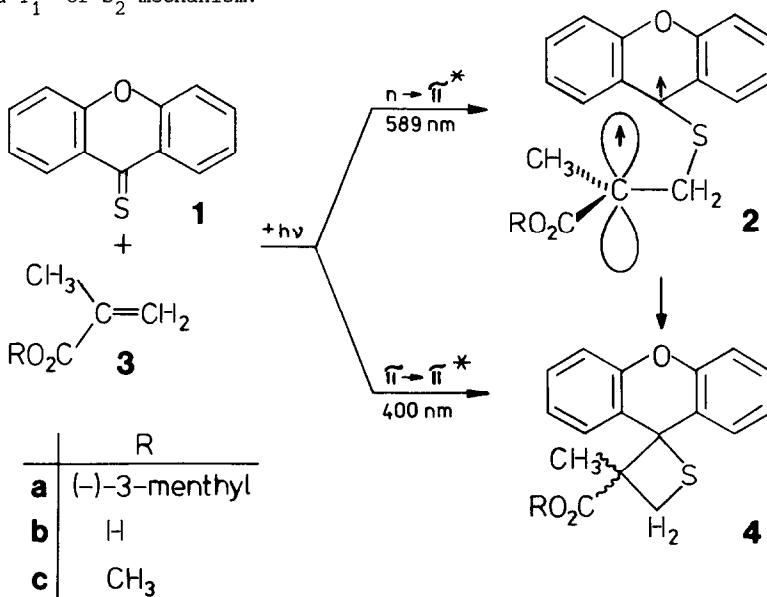
DEPENDENCE OF THE OPTICAL INDUCTION ON THE
 MECHANISM OF THE PHOTOCHEMICAL THIETANE FORMATION

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Abstract: The photochemical thietane formation from **3a** and **1** or **5** proceeds with 3 to 4.5 times higher optical purity via the T_1 state of the thiones than via the S_2 state.

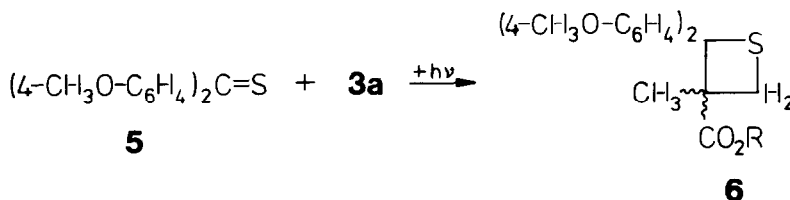
It has been established that xanthione (**1**) reacts upon excitation ($\lambda \approx 400$ nm) to the S_2 state (π, π^* singlet) with electron-poor CC double bonds such as dimethyl maleate or fumarate via an electrocyclic [$\pi_2^2 + \pi_2^2$] process with stereospecific formation of dimethyl *cis*- or *trans*-spiro[thietane-2,9'-xanthene]-3,4-dicarboxylate, respectively¹. On the other hand, when xanthione is irradiated with yellow light ($\lambda = 589$ nm) which populates the T_1 state (n, π^* triplet), reactions with the same substrates lead to non-stereospecific formation of the aforementioned thietanes because of the involvement of biradical intermediates¹. In this communication we wish to report on the optical induction in this preparatively valuable thietane synthesis, using an optically active olefinic substrate, and its dependence on the above mentioned T_1 - or S_2 -mechanism.



Thus, $n \rightarrow \pi^*$ excitation of xanthione (**1**, 0.06 M in benzene) with yellow light ($\lambda = 589$ nm) in the presence of (-)-3-menthyl methylacrylate (**3a**, 0.30 M, $[\alpha]_D^{20} = -96.3^\circ$ (benzene)) proceeds with formation of diastereomeric spiro[thietane-2,9'-xanthene] derivatives **4a** almost

quantitatively (oil: IR (CCl_4), 1725 cm^{-1} (C=O); $^1\text{H-NMR}$ (CCl_4) δ , 0.10-1.93 (m, 21 H), 2.57, 4.05, and 2.60, 4.05 (2 AB, $J = 9.6\text{ Hz}$, CH_2), 6.87-7.40 (m, 6 aromatic H), 7.90-8.33 (m, 2 aromatic H)). Surprisingly, the two high-field doublets of the AB-systems appeared in the $^1\text{H-NMR}$ -spectrum with an area ratio of 59:41 reflecting the distribution of the diastereomeric isomers of 4a which are formed. Alkaline hydrolysis of 4a to the acid 4b, followed by treatment with diazomethane gave a 37% yield of the optically active methyl ester mixture 4c which showed a specific optical rotation of $[\alpha]_{\text{D}}^{20} = +7.5^\circ$ (CCl_4). After complexation of the mixture 4c with the optically active NMR shift reagent $\text{Eu}(\text{TFC})_3$, the low-field part of the AB spectrum appeared as two doublets with a ratio of 58:42; therefore, after hydrolysis the ratio of the enantiomers 4c is still the same as the initial diastereomeric mixture 4a. As expected, the NMR spectrum of racemic 4c, prepared independently from 1 and methyl methacrylate (3c) and complexed with $\text{Eu}(\text{TFC})_3$, exhibited low-field doublets in the 1:1 ratio. These results show clearly that the optical induction reaction via the triplet n, π^* -state of 1 proceeds with 17% optical purity and that the induced chirality causes the opposite optical rotation direction as the asymmetric (-)-3-menthyl initiator group.

On the other hand, $\pi \rightarrow \pi^*$ excitation of 1 with blue light ($\lambda \approx 400\text{ nm}$) in the presence of 3a yielded a diastereomeric 53:47 mixture of 4a, corresponding to an optical purity of 6%.



The analogous light-induced [2+2] cycloaddition reactions of 4,4'-dimethoxy thiobenzophenone (5) with 3a using yellow light (n, π^* triplet) lead to formation of the optically active thietane derivative 6a in 18% optical purity, whereas with blue light (π, π^* singlet) the optical purity of 6a was only 4%. 6a (62%): IR (CCl_4), 1723 (C=O); $^1\text{H-NMR}$ ($[\text{D}_6]$ acetone) δ , 0.27-2.00 (m, 21 H), 2.67, 4.20, and 2.67, 4.23 (2 AB, $J = 9.0\text{ Hz}$, CH_2), 3.73, 3.83 (2 s, 2 OCH_3), 4.5 (m, 1 H), 6.63-7.50 (m, 8 aromatic H).

The optical purity of the thietanes obtained via a triplet n, π^* mechanism is remarkably higher than that formed by the synchronous cycloaddition route involving the S_2 state (π, π^*) of 1 or 5. Perhaps rotation about the CC single bond in the biradical triplet intermediate of type 2 allows closure to the 4 membered ring to occur preferably by the lowest energy pathway and thus increases the selectivity of the reaction. The synchronous reaction pathway from the S_2 state does not involve such a rotation.

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REFERENCES

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