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ON THE QUESTION OF THE LIGHT-INDUCED REACTIVITY OF XANTHIONE IN THE S_2 AND T_1 STATES TOWARDS ELECTRON-POOR AND ELECTRON-RICH ALKENES

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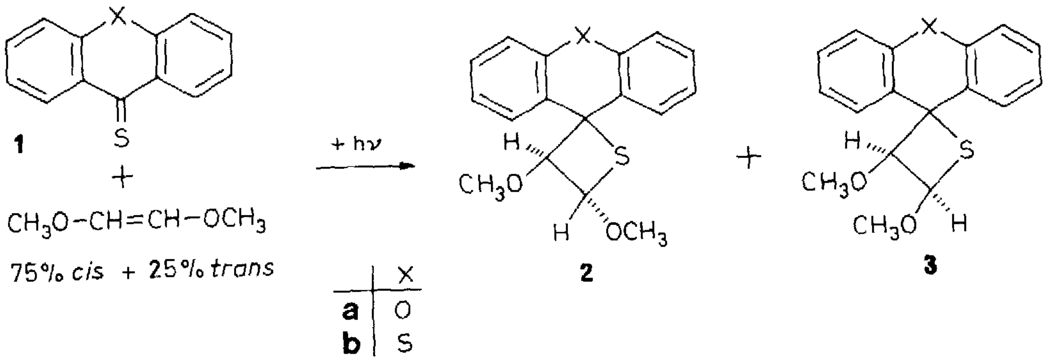
Since the light-induced chemistry of thiones in the presence of unsaturated substrates is of growing interest[1], we wish to report at this stage on the difference in reactivity of xanthione in its S_2 and T_1 states towards electron-poor and electron-rich olefins.

Several years ago we have established that xanthione (1a) reacts upon excitation to the S_2 state (π,π^* singlet) with *electron-poor* CC double bonds, like dimethyl maleate or fumarate, under stereospecific formation of the *cis*- or *trans*-3,4-bismethoxycarbonylspiro[thietane-2,9'-xanthene], respectively[2]. We have interpreted these results on the basis of conservation of orbital symmetry as a photochemically allowed electrocyclic $[{}_\pi 2_s + {}_\pi s_s]$ process. This unusual intermolecular reactivity of 1a in the S_2 state has been explained in terms of the small Franck-Condon factor which results from the relatively large energy gap between the S_2 and S_1 states[3]. The quantum yield for the disappearance of 1a in the presence of dimethyl maleate (0.4 m) was found to be 0.005. The corresponding value with fumarate amounts to 0.048, meaning that fumarate is ten times more efficient than the maleate isomer[3]. More recently, the expected $S_2 \rightarrow S_0$ fluorescence of 1a has been found[4]. On the other hand, the reaction of xanthione in the T_1 state (n,π^* triplet) with the same substrates proceeded with non-stereospecific formation of the above-mentioned thietanes, as a result of a slower reaction via biradical intermediates[2].

In contrast to these previous findings, the reaction of xanthione upon $n \rightarrow \pi^*$ as well as $\pi \rightarrow \pi^*$ excitation in the presence of a 75:25 mixture consisting of *cis*- and *trans*-1,2-dimethoxy-ethylene yields a stereochemically reversed product ratio, namely 75% *trans*-dimethoxy-thietane 2a (mp 99-99.5°) together with 25% of the *cis*-isomer 3a (oil). The structures of these compounds can be assigned on the basis of chemical shift differences in the nmr spectra[5]. The latter results indicate that the photocycloadditions of 1a with *electron-rich* CC double bonds proceed non-stereospecifically through the T_1 state of 1a. Quenching constants of the 1a phosphorescence with diethoxy-ethylenes and other unsaturated substrates have very recently been published[6].



Similarly, the light-induced reaction of thioxanthione (1b) with 1,2-dimethoxy ethylene (75% *cis* + 25% *trans*) using sodium light (n→π* excitation) produces 2b (mp 131-132.5°) and 3b (oil) in a 78:22 ratio.

We explain these differences in reactivity of 1a, upon excitation to the S_2 state, towards electron-poor and electron-rich alkenes in a first-order approximation in terms of molecular orbital interaction diagrams[7], as shown in figure 1. The bonding levels in the diagrams are placed in accordance with photoelectron spectroscopy measurements, and the higher energy levels are positioned on the basis of electronic excitation energies[8].

In the case of dimethyl maleate, the dominant orbital interaction is between the π*-orbitals of maleate and 1a in its S_2 state. Since this interaction possesses also favorable orbital phase overlap, a concerted $[_\pi 2_s + _\pi 2_s]$ *cyclo-addition* with stereospecific retention can be predicted. On the other hand, the interaction between the π-orbital of the maleate and the n-orbital of 1a, in its n,π*-state, should be very small on the basis of the 2.4 eV energy gap. Consequently, xanthione should react with maleate substantially faster in the S_2 state than in the S_1 or T_1 state.

In the case of 1,2-dimethoxy-ethylenes, however, the situation is reversed. Since the methoxy groups raise both filled and vacant levels, the interaction of the π*-orbital of 1a in the S_2 state with the π*-orbital of dimethoxy-ethylene is very poor. Therefore, the intermolecular chemical reaction from the S_2 state of 1a towards dimethoxy-ethylene can be neglected. The most important process is now the radiationless deactivation of the S_2 state by way of internal conversion and intersystem crossing to the T_1 state (n,π* triplet). In this case, the dominant interaction now involves the filled π-orbital of the dimethoxy-ethylene and the singly occupied n-orbital of 1a in the n,π*-state, which facilitates the formation of a biradical intermediate. Consequently, the reaction rate of 1a with electron-rich olefins should be accelerated by

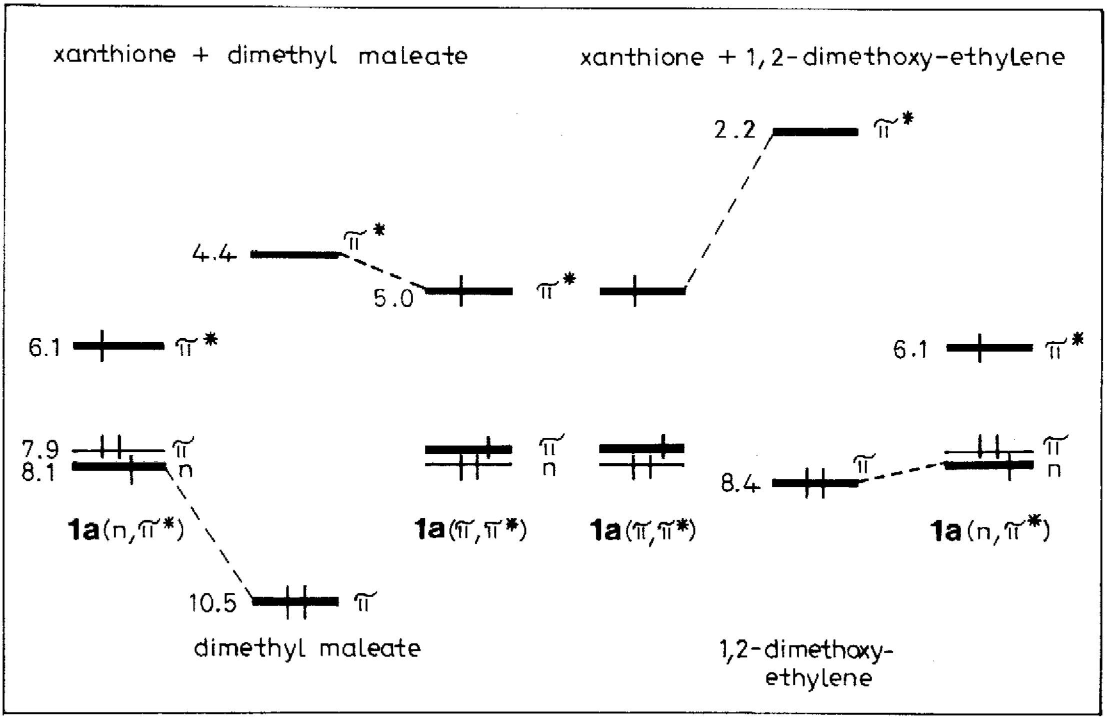


Figure 1. Molecular orbital interaction diagrams of 1a with dimethyl maleate and 1,2-dimethoxy-ethylene.

a large factor in the T_1 state, as compared to the S_2 state.

Even the tenfold increase in reactivity of 1a in the S_2 state with fumarate over that with maleate can be explained with the interaction diagrams of figure 2. The energy gap between the involved π*-orbitals is 0.4 eV smaller in the case of fumarate than in the case of maleate, from which one would predict that fumarate should be slightly more reactive against 1a in the S_2 state than maleate. The excellent agreement of these predictions, neglecting orbital coefficients, with our experimental findings is remarkable.

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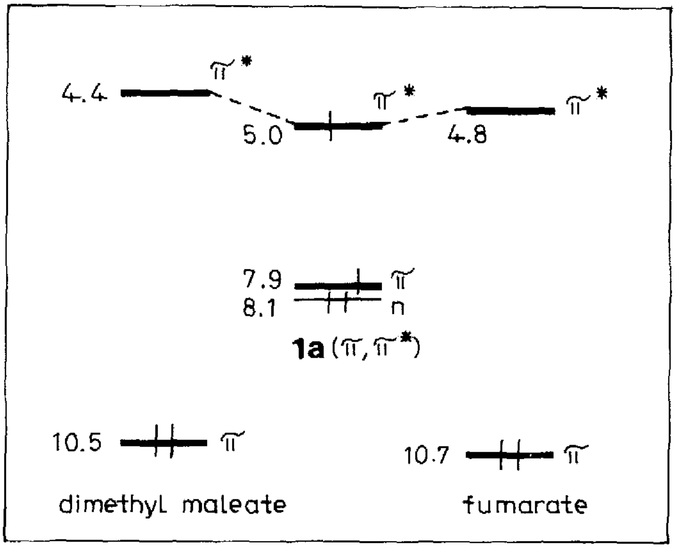

Figure 2. Molecular orbital interaction diagrams of 1a in the S_2 state with dimethyl maleate and fumarate.

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8. The effects of configuration interaction then cause the π* levels in the center of figure 1 artificially to appear at a different place than at the left and right. This type of representation has the advantage, however, that we can use one-electron perturbation arguments throughout.