

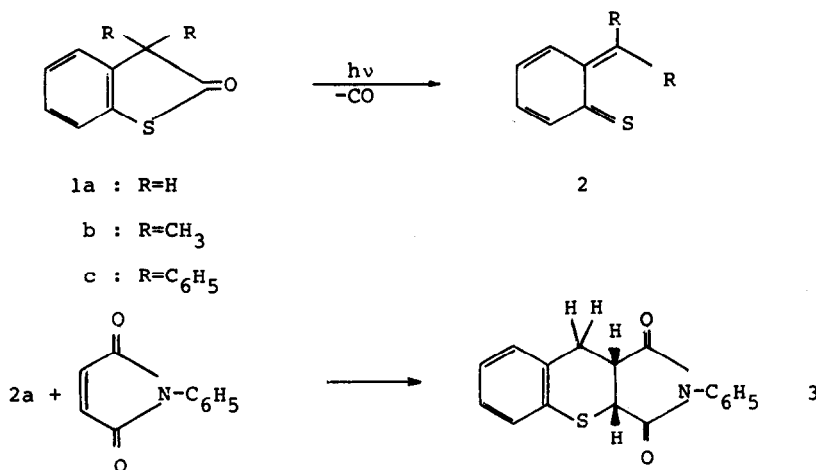
EVIDENCE FOR AN *ORTHO* QUINOID INTERMEDIATE IN THE PHOTOCHEMISTRY
OF 2-(3H)-BENZO[b]THIOPHENONE

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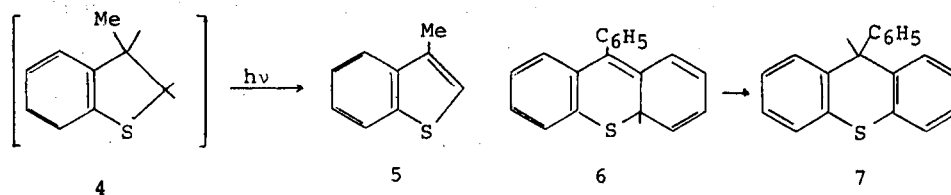
Conjugated thiones are formed by irradiation of thio- and dithio-carbonates^{1,2}; we have now found that similar structures are also formed from thiolactones. When 2-(3H)-benzo[b]thiophenone 1a is photolysed (in benzene or cyclohexane, vacuum degassed; medium pressure Philips HPK 125 mercury arc) in the presence of N-phenylmaleimide, adduct 3 is formed in a very high yield³; it was purified by chromatography through silicagel (ether) and sublimed (m.p.: 167-168°C). Minor by-products are a maleimide dimer (in benzene) or N-phenylsuccinimide (in cyclohexane).



Adduct 3 shows a parent peak at $m/e = 395$ and an IR band at 1700 cm^{-1} . The aliphatic part of the NMR spectrum (CDCl_3 , 100 MHz) is an ABXY pattern with the following parameters (shifts in ppm downfield from TMS): $\delta_A = 3.35$,

$\delta_B=3.03$, $\delta_X=3.76$, $\delta_Y=4.25$; $J_{AB}=13.9$ Hz, $J_{AX}=5.7$ Hz, $J_{BX}=3.4$ Hz, $J_{XY}=9.5$ Hz; this spectrum is very similar to the one found for the adduct of maleic anhydride to the *ortho* quinoid intermediate photogenerated from 2-methylbenzophenone⁴. This appears to be the first example of a 2+4 cycloaddition to a "diene" containing a sulphur atom.

When 1b or 1c are irradiated in the same conditions, no adduct could be detected, neither with N-phenyl maleimide nor with dimethyl acetylenedicarboxylate, even in 0.5 molar solutions of dienophile. The only products isolated suggest that the corresponding intermediates (2b or 2c) are formed, and that they undergo very rapid intramolecular reactions. Actually, 2b gives 3-methyl-benzo[b]thiophene 5; there is some precedent for structures similar



to 4 being easily aromatised under irradiation⁵, making 4 an attractive intermediate in the formation of 5. This dihydro compound can be visualised as resulting from a [1-5] sigmatropic hydrogen shift yielding *ortho*isopropenylthiophenol, followed by a cyclisation. Similarly⁶, 2c has been suggested to undergo an electrocycloisatation to 6 which then isomerises to the isolated product 7.

Intramolecular pericyclic reactions of the quinoid intermediate 2 compete thus quite efficiently with intermolecular trapping, pointing to a high reactivity of the doubly bonded sulphur atom.

References

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