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PHOTOCHEMISTRY OF DIARYL SUBSTITUTED 1,2-DITHIOLYLIUM SALTS.

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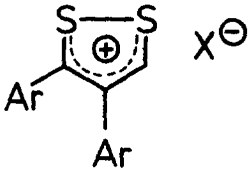
The photochemical behaviour of 1,2-dithiole derivatives has hitherto received very little attention (2,3). We report results of the study of the photochemical reactions of the two types of diaryl substituted 1,2-dithiolylium salts (I and II), which clearly show the importance of the substitution pattern on determining the reaction pathways.

I



II

Flash photolysis (4) of I in 96% EtOH either in the presence or absence of air gave two compounds, a short lived one with a relaxation time of 0.70 ms and a more long lived one with a relaxation time of 1.0 s (5). The absorption spectra of the two products are shown in Fig. 1.

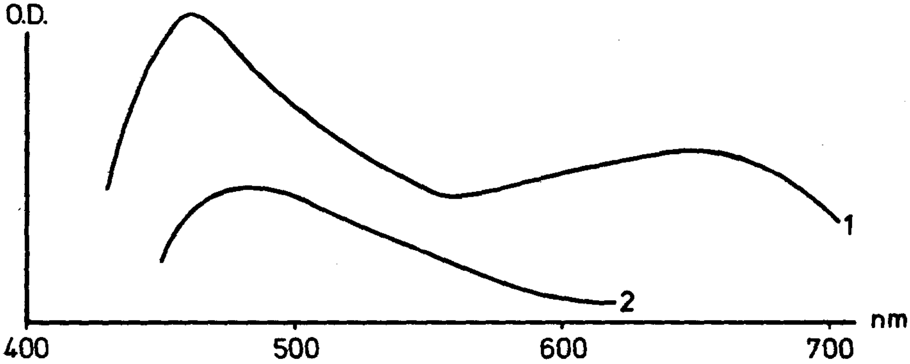
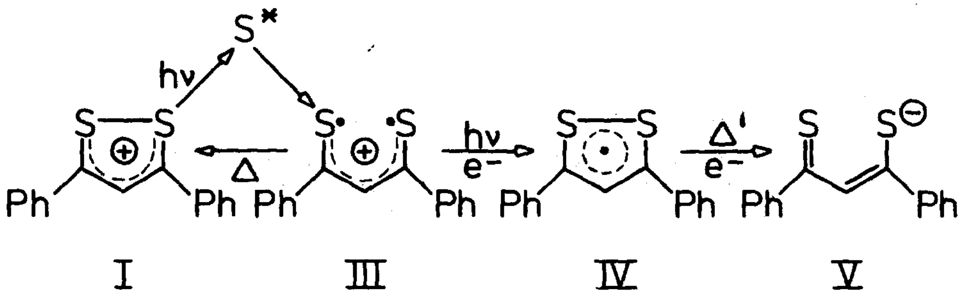


Fig 1. Absorption spectra of photoproducts derived from I. 1 Short lived product, 2 long lived product.

It has been shown that 1,2-dithiolylium salts of type I give rise to stable radicals of the type IV on cathodic reduction in MeCN (6). The absorption spectrum of the short lived product (7) is identical to the absorption spectrum of IV (8) indicating that it is a dithiolyl radical formed via a photoreduction involving the solvent.

The absorption spectrum of the long lived product was found to be identical to that of the dithioketonate ion (V) which has recently been characterised as the one electron reduction product of the stable radical, IV (8).

Based on the experimental observations depicted below, we propose the following mechanism for the formation of the dithiolyl radical and the dithioketonate ion.



The kinetics were unaffected by the presence of oxygen. Although conclusions based on the effect of oxygen on the excited state should be exercised with care, this is in agreement with a mechanism in which the photoproduct arises from an excited singlet state.

The formation of IV is a biphotonic process. The quantum yield for the formation of IV was found to be proportional to the square of the light intensities from the flash lamps. Thus a photochemical formed intermediate in between I and IV undergoes a further photochemical reaction competitive with a thermal reaction (9).

IV decays into V by a thermal process. At 650 nm where V does not absorb the decay of IV was a first order process with $k = 1400$ sec^{-1}. At wavelength where both IV and V do absorb the apperent rate constant, for the decay of IV was found to be smaller and proportional to the absorption of V and obeyed higher order kinetics. This is what should be expected if IV decays into V. The decay rate of IV was independent of the light intensities employed, which means that the decay is a thermal process. Furthermore the quantum yield for the formation of V was found to be proportional to the square of the light intensities, which supports the conclusion that the process IV → V is thermal.

Finally we propose structure III for the intermediate in going from I to IV. This is in analogy with the photochemical reaction of simple disulfides in which the primary process consists of a cleavage of the disulfide bond with formation of thiyl radicals (10). In the present case the lifetime of the biradical III cannot be more than 10^{-5} sec., due to the fact that the photochemical forward reaction to IV was able to compete with the thermal back reaction within the duration of the flash.

The dithiolylium salts of type II showed a short lived product with a relaxation time of 6 ms and a long lived product which decays with a first order rate constant equal to 0.88 sec^{-1}. The absorption spectra of the two products are shown in Fig. 2.

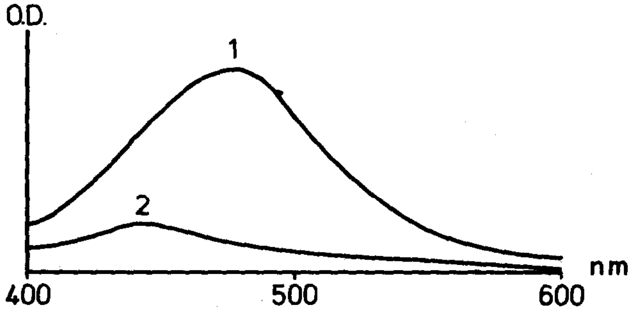
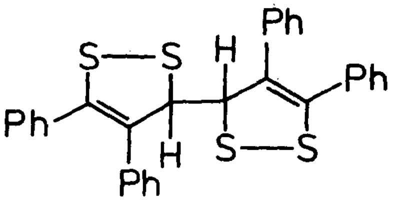


Fig. 2. Absorption spectra of photoproducts derived from II. 1 Long lived product, 2 short lived product.

The band at 480 nm in the spectrum of the long lived product is characteristic for dithioketonate anions (11). The dithioketonate anion has not been observed by cathodic reduction of 3,4-diaryl substituted 1,2-dithiolylium ions. This reduction resulted in the formation of the stable dimer VI (12) which does



VI

not absorb at 480 nm.

On irradiation of solution of II for longer periods, no change of the absorption spectrum could be observed, indicating that the products observed by flash photolysis revert to the starting material by a dark process.

Photolysis of salts of type I and II substituted with other aryl groups showed analogous behaviour.

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