# Photochemically-induced *cis–trans*-Isomerisation of α-(1,2-Dithiol-3-ylidene) Ketones

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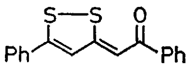
*Summary* Aryl-substituted α-(1,2-dithiol-3-ylidene)ketones have been shown to give *trans*-isomers and not O–S bonded valence tautomers upon photolysis.

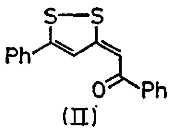
As part of our studies of the photochemistry of 1,2-dithiole derivatives we have examined the photolysis of aryl-substituted α-(1,2-dithiol-3-ylidene) ketones,[1] and report here that (I) is transformed into the *trans*-isomer (II) and not into the O–S bonded isomer (III), as described by Gleiter *et al.*[2] for the photolysis of (IV). It has been shown by core-electron spectroscopy that O–S bonded forms do not contribute to the ground state of dithiolylidene ketones.[3]

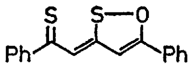
We have observed that the absorption spectrum of an irradiated solution of (I) in 96% ethanol is dependent on the time between the irradiation and the recording of the spectrum. Flash photolysis[4] of $10^{-7}$M-solutions in 96% ethanol and cyclohexane showed the formation of a compound which reverted to starting material by a dark process obeying first-order kinetics with $k_{\mathrm{EtOH}} = 3{\cdot}1 \times 10^{-3}\ \mathrm{s}^{-1}$ and $k_{\mathrm{cyclohexane}} = 1{\cdot}3 \times 10^{-4}\ \mathrm{s}^{-1}$. The light energy necessary to produce transformation of (I) is so low that 30 ml of a $10^{-7}$M-solution was totally converted into the photo-product by a 100 W iodine–quartz lamp, so that a subsequent flash did not augment the concentration of the photo-product.

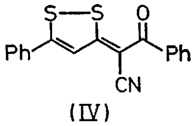
The quantum yield for the formation of the photo-product was found to be independent of the presence or absence of oxygen. Although conclusions based on the effect of oxygen on the excited state should be made with care, this observation is consistent with the hypothesis that the photo-product is formed *via* an excited singlet state. The observed lifetime of the photo-product precludes the compound formed being in an excited state. Thus the photo-product appears to be an isomer of the starting material.

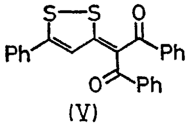
A $10^{-7}$M-matrix of (I) in poly(methyl methacrylate) kept in the dark showed an absorption spectrum similar to that of I) in ethanol. When this matrix was exposed to high energy u.v. light a photo-product was formed which had an absorption spectrum similar to that of an irradiated ethanolic solution of (I). However, the photo-product was found to be stable in the matrix at room temperature and only during prolonged heating at 110° reverted to starting material. This means that the high energy induced forward process to some extent is still able to proceed in the matrix, but the thermal back process cannot due to the increased viscosity of the solvent. The influence of the polarity of the solvent can be ruled out, as the above-mentioned effect is not observed in ethyl acetate solutions. The formation of (II) and the corresponding dark process, which changes the geometry of the molecule drastically should be dependent on the viscosity of the solvent. However, the formation of an O–S bonded valence tautomer only requires small changes in the geometry of the molecule, *i.e.*, the isomerisation and the thermal back process should be independent of the viscosity.

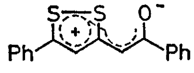

(I)


(II)


(III)


(IV)


(V)


(VI)

On the basis of this we conclude that the photo-product of (I) is the *trans*-isomer (II). This assumption is further supported by the fact that (V),[5] which is invariant to *cis–trans*-isomerisation around the exocyclic double bond, but is able to form an O–S bonded isomer, is photostable in ethanol and cyclohexane. The stability was checked at 10 nm intervals in the 400—500 nm region.

The lifetime of an O–S bonded tautomer of (V) could be diminished below the detectable value in ethanol due to hydrogen bonding but this can be ruled out in cyclohexane solution.

*It is known* that dipolar forms such as (VI) contribute to the structure of dithiolylidene ketones.[1,3] The contribution of such forms lowers the barrier of rotation around the exocyclic double bond. As the contribution of dipolar forms are more pronounced in polar solvents, this may explain the difference in the lifetime of the photo-product in ethanol and cyclohexane. Gleiter *et al.*[2] observed both a short and a long lived product in the photolysis of (IV); we have only observed a long lived product in the photolysis of (I). The absorption spectrum of this is only slightly different from that of (I) (increased absorption at 500 nm, isosbestic points at 480 and 430 nm).

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[1] For a recent review of dithiolylidene ketones see N. Lozac'h, *Adv. Heterocyclic Chem.*, 1971, **13**, 161.

[2] R. Gleiter, D. Werthemann, and H. Behringer, *J. Amer. Chem. Soc.*, 1972, **94**, 651.

[3] B. J. Lindberg, S. Högberg, G. Malmsten, J.-E. Bergmark, Ö. Nilson, S.-E. Karlson, A. Fahlman, U. Gelius, R. Pinel, M. Stavaux, Y. Mollier, and N. Lozac'h, *Chemica Scripta*, 1971, **1**, 183.

[4] Conventional flash kinetic equipment was used, see G. Porter in 'Technique of Organic Chemistry,' ed. A. Weissberger, Interscience New York, 1963, vol. **8**, part II, p. 1055. The flash lamps were filled with air. The decay rates were reproducible to ±5%.

[5] Y. Mollier, F. Terrier, R. Pinel, C. Menez, and N. Lozac'h, *Bull. Soc. chim. France*, 1967, 2074.